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XXI. *An X-Ray Examination of i-Erythritol.*

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THE present paper deals with the X-ray examination of an organic compound of relatively simple constitution, *i*-erythritol,

$$CH_2.OH—\overset{*}{C}H.OH—\overset{*}{C}H.OH—CH_2.OH.$$

The investigation was undertaken mainly to determine the symmetry of the crystal-molecule. Erythritol is one of the simplest compounds with two so-called "asymmetric" carbon-atoms (indicated in the formula by asterisks), and moreover two which are linked with exactly similar groups of atoms. A difference in the spatial arrangement of these groups with regard to the "asymmetric" carbon-atoms is possible. This gives rise to the existence of a right-handed and a left-handed form, a racemic form, and an internally-compensated or meso form. The compound is wholly comparable with tartaric acid.

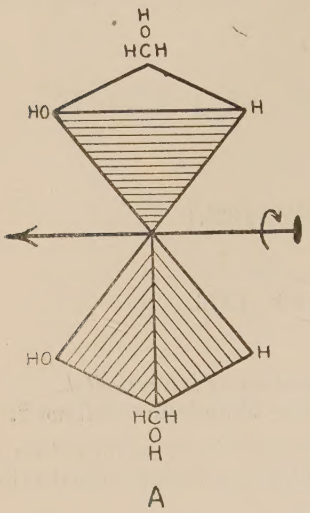
In figs. 1 and 2 the different forms are represented in the usual schematic way. The "asymmetric" carbon-atoms (which are not represented in the figures) occupy corresponding positions within the tetrahedra. According to the conventions of stereochemistry, the configurations in these figures are drawn in the most symmetrical way.

A and B are two possibilities of the same active form (B has been obtained from A by rotating the upper tetrahedron through 180° about the bond between the two

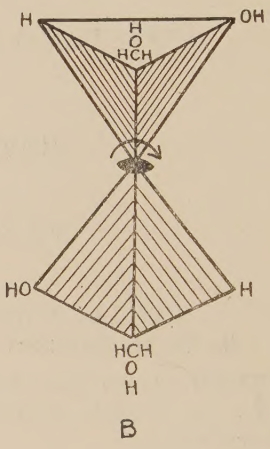
* Communicated by Sir William Bragg, K.B.E., F.R.S.

asymmetric carbon-atoms). They have a two-fold axis as the only symmetry-element, and are therefore different from

Fig. 1.

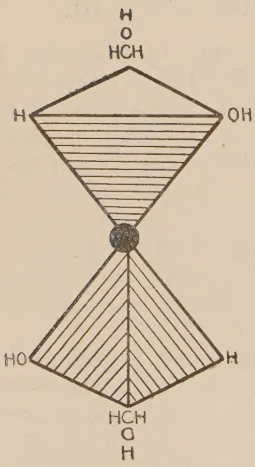


A

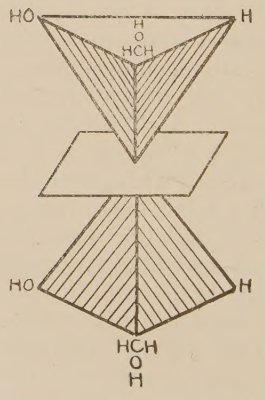


B

Fig. 2.



C.



D.

their mirror-images * : A and B thus represent either *di*- or *l*-erythritol.

* *Cf.* F. M. Jaeger, 'Lectures on the Principle of Symmetry and Its Applications in all Natural Sciences'; and also F. M. Jaeger, *Rec. Trav. Chim. des Pays-Bas*, xxxviii. p. 174, *et seq.* (1920).

On the other hand, C and D (D has been obtained from C in the same way as B from A) show symmetry of the second kind, viz. C a centre of symmetry, D a plane of symmetry. They are two possible representations of *i*-erythritol.

It is probable that the chemical molecule (the molecule as present in a solvent or in the gaseous state of a substance *) has statistically the most symmetrical configuration which is consistent with its structure. The determination of the symmetry of the crystal-molecule (the molecule which is present in the crystal †) is often of use in deciding the nature of this "free" symmetry.

In general the crystal-molecule will be less symmetrical than the chemical-molecule, the distortion being due to forces brought into play by the act of the crystallization. It is, moreover, quite conceivable that a more or less symmetric chemical-molecule may lose all its symmetry as a consequence of this process. Therefore it is by no means certain that a definite symmetry element which may well be present in the "liquid" state will be found in the crystalline state. But it is fairly safe to assume that if a crystal-molecule proves to have a certain element of symmetry, that same element will be present in the chemical-molecule, perhaps accompanied by other symmetry elements. X-ray analysis of organic compounds reveals the fact that the symmetrical crystal-molecules very often show symmetry properties which could have been deduced as "possible" from the stereochemical configuration. This may be seen from a few examples :—

Benzene ‡, naphthalene §, and anthracene § have probably a centre of symmetry; the same holds for hexachlorbenzene ‡, hexabrombenzene ‡, and oxalic acid ‖. Urea ‡ has two perpendicular planes of symmetry intersecting in a two-fold axis, while symmetrical di-methylurea ‡ has one plane of symmetry (monomethylurea ‡ is asymmetric). Hexamethylenetetramine ** shows all the symmetry properties of its stereochemical configuration. In these cases and in

* Sir W. H. Bragg, "The Significance of Crystal Structure," J. Chem. Soc. cxxi. p. 2766 (1922).

† *Loc. cit.*

‡ H. Mark. *Ber. d. Deutschen Chem. Ges.* lvii. p. 1820 (1924).

§ Sir W. H. Bragg and W. L. Bragg, 'X-Rays and Crystal Structure, 4th Edition, p. 252.

‖ H. Hoffmann und H. Mark, *Ztf. für Physik. Chem.* cxi. p. 321 (1924).

¶ H. W. Gonell und H. Mark, *Ztf. für Physik. Chem.* cvii. p. 181 (1923).

** R. G. Dickinson, J. Am. Chem. Soc. xlv. p. 22 (1923).

many others the possible stereochemical symmetry has wholly or partly been retained in the crystal *. The greater the number of symmetry elements of the chemical-molecule, the greater will be the probability that some at least of these elements will appear in the crystal-molecule.

i-Erythritol crystallizes in the tetragonal bipyramidal class †. It forms well-developed crystals, often of considerable size. The crystallographic data are given by Groth‡ :—

$$a : c = 1 : 03762.$$

Two values are given for the density. They show a considerable difference, viz. 1·590 § and 1·450 ‖. A re-determination by the suspension-method, using as liquid a mixture of carbon tetrachloride ($\rho = 1{\cdot}593$) and benzene ($\rho = 0{\cdot}88$), gave $\rho = 1{\cdot}441$.

A small section of a crystal was used in this work. Its size was about $6 \times 3 \times 0{\cdot}8$ mm. A Bragg ionization spectrometer with a Coolidge X-ray bulb of molybdenum anticathode was used to measure the spacings, and also relative intensities of the different orders of a few principal planes. Also powder and rotation photographs were taken with copper rays.

The crystal-section was cut parallel to the *c*-axis. It was found that the plane of the surface exposed was neither the (100) nor the (110) plane. X-ray measurements showed that a prism-plane, making an angle of 45° with the plane of the section, had the same spacing as another prism-plane at a corresponding angle of 8° 8′, both angles being measured in the same direction. These two equally-spaced sets of planes must be symmetrically disposed about either the (100) or the (110) plane, and make an angle of $1/2 \times (45° - 8° 8') = 18° 26'$ with one of them. The (100) plane has been chosen here. The two prism-planes in the tetragonal system which make an angle of 18° 26′ with the (100) plane are the (310) and the ($\bar{3}10$) plane. The plane of the crystal section itself makes an angle of 26° 34′ with the (100) plane, and is therefore the (210) plane. If the (110) plane is

* However, it should be noted that, *e. g.* in penta-erythritol (*cf.* note *, p. 291) the crystal-molecule possesses a four-fold rotation axis, whereas from a stereochemical point of view a more tetrahedral arrangement would appear probable.

† For a confirmation by Laue-photographs, see H. Haga and F. M. Jaeger, Proc. Roy. Acad. of Amsterdam, xviii. p. 1352 (1916).

‡ 'Chemische Krystallographie,' iii. p. 240.

§ Lamy, *Ann. d. Ch.* (3) xxxv. p. 139.

‖ Schröder, *Ber. d. Deutschen Chem. Ges.* xii. p. 562 (1879).

chosen instead of the (100), the indices of the planes (210) and (130) are interchanged.

The following spectrometer measurements of a number of planes of the crystal were made (Table I.). The value of

TABLE I.

Plane.	Spacing (Å.).		Remarks on relative intensities of successive orders.
	Observed.	Calculated.	
(100) ...	6·38	12·76	II. weak; IV. and VI. strong; VIII.>II.
(110) ...	4·50	9·02	II. very strong; II.>IV.>VI.>VIII.
(210) ...	2·86	5·71	
(310) ...	2·02	4·03	
(410) ...	1·55	3·09	
(510) ...	1·26	2·50	
(710) ...	*	1·81	
(320) ...	1·77	3·54	
(520) ...	1·18	2·37	
(430) ...	1·28	2·55	
(530) ...	1·09	2·19	
(730) ...	*	1·68	
(540) ...	1·00	1·99	
(750) ...	*	1·48	
(970) ...	*	1·12	
(001) ...	1·71	6·83	IV. moderately strong; IV. ⩾VIII.
(101) ...	6·03	6·02	I. and II. strong; II.>I.⩾IV.>III.
(301) ...	3·62 †	3·61	
(111) ..	2·73	5·44	II. strong; II.⩾IV.
(211) ...	4·40	4·38	
(311) ...	1·74	3·47	
(321) ...	3·14 †	3·14	

* Of these planes no reflexions could be found corresponding to the calculated spacings after careful examination. The second orders could not be found, obviously because the glancing angles became very large, viz. 23°, 25°, 28¾°, 39½° respectively.

† Calculated from a rotation photograph.

the spacing in the direction of the *a*-axis was determined by taking a rotation photograph with the *a*-axis as axis of rotation; it was found to be 12·74 Å. For the *c*-spacing was found in the same way 6·80 Å. From the spectrometer measurements can be deduced for these two spacings 12·76 Å and 6·83 Å respectively. The spacings of all planes in the table were calculated with the latter two values of *a* and *c*.

The spacing of the basal plane is quartered; all planes of the prism zone show halved spacings, and also those planes

(hkl) for which $(h+k+l)$ is odd. This was confirmed by a rotation photograph about the c-axis (Table II.).

TABLE II.

Indices of spots.	Obtained spacing in Å.	Calculated spacing in Å.
(220)	4·53	4·51
(420)	2·83	2·86
(440)	2·22	2·25
(101)	6·10	6·02
(211)	4·40	4·38
(301)	3·62	3·61
(321)	3·14	3·14
(112)	3·19	3·19
(202)	3·00	3·01
(222)	2·72	2·72
(332) }	2·23	2·26
(422) }		2·19

In the last two columns are given the spacings of the planes as obtained from the photograph and as calculated for a cell with $a=12{\cdot}76$ Å and $c=6{\cdot}83$Å.

It should be noted that, while (222) was a very distinct spot, (111) was absent; (311) was also absent.

The observed quartering and halvings are in this class characteristic of the space-group C^6_{4h}, the fundamental lattice being the body-centred tetragonal lattice Γ_t' *.

From the above results the number of molecules per unit-cell is 8 (7·96).

As has been already stated, all measurements were made with a small crystal section, and the choice between the (100) and (110) planes was arbitrary. A well-developed crystal on which appeared the face described by Groth as (100) was examined on the spectrometer, and it was found that this plane corresponded to the (110) of the cell chosen above. This means that in the description used by Groth the crystal is referred to a face-centred lattice Γ_f'. In the tetragonal system this is geometrically equivalent to the body-centred lattice, which has been used in this investigation. The elementary parallelepiped has the same height in the two cases, but the side of the basal plane of the face-centred cell is the diagonal of the basal plane of the body-centred cell. It is easily seen that the necessary transforma-

* W. T. Astbury and Kathleen Yardley, "Tabulated Data for the Examination of the 230 Space-groups by Homogeneous X-rays," Phil. Trans. Roy. Soc. A, ccxxiv. p. 239 (1924).

tion of the axial ratio used here (body-centred cell) reproduces that of Groth (face-centred cell).

The number of asymmetric bodies necessary for the construction of a body-centred unit-cell in the tetragonal bipyramidal class is 16 ; this means that sixteen asymmetric molecules can be disposed about the elements of symmetry in such a way that the symmetry of the whole is tetragonal bipyramidal. When, as in the present case, the cell contains only eight molecules, the molecules cannot be placed in the most general positions, but each molecule must occupy a special position in the unit-cell and possess two-fold symmetry of its own. The tables of Astbury and Yardley show that the possible molecular symmetry in this case is either a centre of symmetry or a two-fold axis. This conclusion can be easily deduced from a consideration of the diagram * which represents this space-group, in the way described by the authors.

The arrangement of the molecules in the two cases can be seen from figs. 3 and 4, which represent projections

Fig. 3.

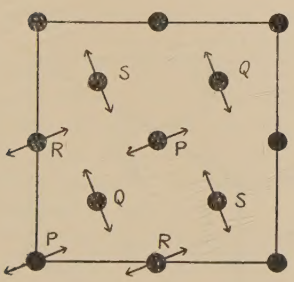
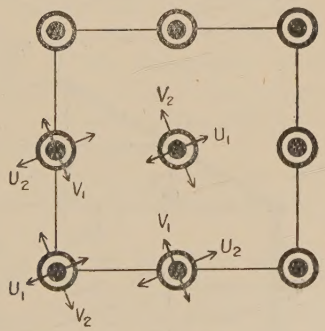


Fig. 4.



on the basal planes of the unit-cells. The positions in th unit-cells themselves are given in figs. 5 and 6.

When the eight molecules are centro-symmetrical (figs. 3 and 5), they are all completely identical in the sense that they can be obtained from each other without recourse to reflexions ; *i.e.* they cannot be described as either right-handed or left-handed. For convenience we may consider them as four pairs, P, Q, R, S, each of these pairs being obtained from the proceding pair by a rotation about a tetragonal axis, followed by a translation of $\frac{c}{4}$.

* *L. c.* p. 223 and Diagram No. 100.

In the other case (figs. 4 and 6) four of the molecules, viz. two U_1 and two V_1, are the mirror images of the other four, viz. two U_2 and two V_2. A U_1-molecule may be obtained from a V_1-molecule by a rotation of 90° about a tetragonal axis, followed by a translation of $\frac{c}{4}$; the same relation holds for U_2 and V_2.

Fig. 5.

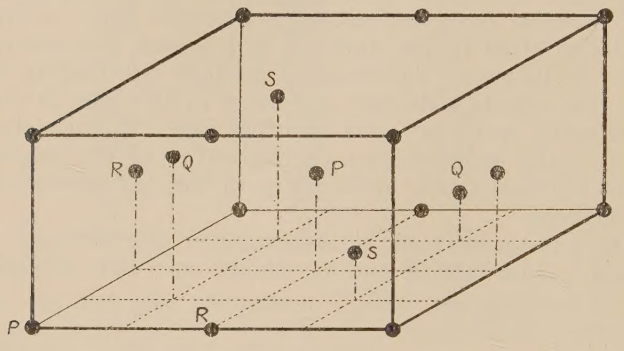
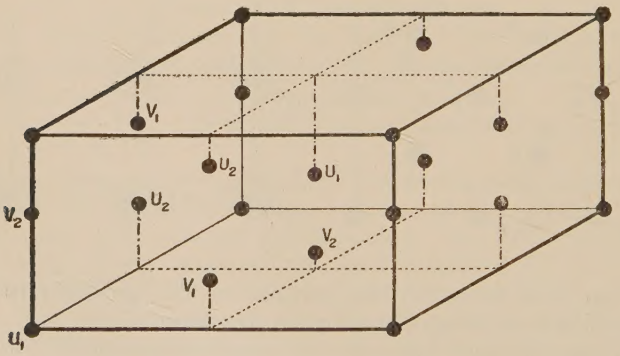


Fig. 6.



The directions of the arrows represent diagrammatically the difference in orientation of the molecules as a consequence of the above-mentioned rotation.

In both cases definite points of the molecules, viz. corresponding points of the two-fold axes of the axially-symmetric molecules and the symmetry-centres of the centro-symmetric molecules, occupy eight equivalent positions in the unit-cell. The coordinates of these positions referred to the edges of the unit-cell can be deduced from the diagram

mentioned above; or they can be found in R. W. G. Wyckoff's 'The Analytical Expression of the Results of the Theory of Space-Groups' *.

When the unit-cells are chosen in such a way that the corners are occupied by molecules, then the coordinates of the 8 centres of the centro-symmetrical molecules are:

$$0\,0\,0;\ \tfrac{1}{4}\,\tfrac{1}{4}\,\tfrac{3}{4};\ \tfrac{1}{2}\,0\,\tfrac{1}{2};\ \tfrac{3}{4}\,\tfrac{1}{4}\,\tfrac{3}{4}$$
$$0\,\tfrac{1}{2}\,0;\ \tfrac{1}{4}\,\tfrac{3}{4}\,\tfrac{1}{4};\ \tfrac{1}{2}\,\tfrac{1}{2}\,\tfrac{1}{2};\ \tfrac{3}{4}\,\tfrac{3}{4}\,\tfrac{1}{4},$$

and the coordinates of the 8 equivalent points of the axially-symmetric molecules are:

$$0\,0\,0;\qquad \tfrac{1}{2}\,0\,\tfrac{3}{4};\ 0\,\tfrac{1}{2}\,\tfrac{1}{4};\ \tfrac{1}{2}\,\tfrac{1}{2}\,\tfrac{1}{2}$$
$$0\,0(\tfrac{3}{4}-2u);\ \tfrac{1}{2}\,0(\tfrac{1}{2}-2u);\qquad 0\,\tfrac{1}{2}\,\overline{2u};\ \tfrac{1}{2}\,\tfrac{1}{2}(\tfrac{1}{4}-2u).$$

It can be seen at once, that while the centres of the centro-symmetric molecules are placed in quite definite positions, one degree of freedom with regard to their positions on the *c*-axis remains for the axially-symmetric molecules.

It is not possible to decide between these two possibilities with such a certainty as accompanies the determination of the space-group and the number of molecules in the unit-cell. However, a consideration of the intensities of the reflexions of a few principal planes, and also of the external form of the crystal, gives strong evidence of the presence of a centre of symmetry in the crystal-molecule.

In what follows the presence of centro-symmetric molecules is indicated as case *a*, the presence of axially-symmetric molecules as case *b*.

The principal planes have the longest spacings, and, as a consequence, the molecules have the largest distance from each other in directions perpendicular to these planes; therefore, in making an approximation of the reflexion intensities of these special planes, it is justifiable in the first instance to consider each molecule as a single scattering centre, at least for the first orders. For the higher orders, and for the reflexions of more complicated planes it is, in most cases, not possible to interpret even roughly the intensities in such a simple way.

In Table III. the approximate relative intensities from successive orders of three planes are given, as found by spectrometer measurements.

The actual numbers given are average values for different observations, and must be considered only as giving a general

* Carnegie Institution of Washington, Publication No. 318.

Table III.

Plane.	Approximate relative intensities from successive orders.							
	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
(100)	...	10	...	65	...	120	...	17
(110)	...	400	...	90	...	10	...	5
(101)	130	160	3	10				

idea of the relative magnitudes of the reflexions. But the conclusions drawn from them and summed up in the following points are beyond any doubt, viz. :—

1. By far the strongest reflexion is given by (110), much stronger than by (100).
2. The IInd order of (100) is very weak, the IVth and VIth orders are strong, the VIIIth order is stronger than the IInd.
3. The (101) plane gives strong Ist and IInd orders, the IIIrd order is very weak, the IVth order stronger than the IIIrd.

The two possible arrangements of the molecules with regard to the main prism-planes (100) and (110) can be easily seen in figs. 3 and 4. They show obviously that the experimental results (1) and (2) are in general agreement with fig. 3, *i. e.* case *a*. Indeed, in fig. 3 the (110) plane is more closely packed with molecules than the (100) plane, while in fig. 4 the converse is true. So in case *a* we expect (110) to be the stronger reflecting plane ; in case *b*, on the contrary, (100).

And further, in fig. 3, the (100) planes which carry P and R molecules are half-way interleaved by planes carrying Q and S molecules ; a similar arrangement does not occur in fig. 4. Therefore, in case *a* a weak IInd order and a strong IVth order can be expected, and are actually found. The VIth order is also very strong, and although this may seem to be strange, it is not necessarily contradictory to the conclusions already drawn. In fact, since the molecules are in reality groups of scattering atoms, and are, moreover, differently orientated with regard to the successive (100) planes, it is quite possible that, although certain atoms of the Q and S molecules will weaken the rays scattered by certain

atoms of the P and R molecules in both the IInd and the VIth orders of (100), other atoms will reinforce each other in the VIth order only. If there were no difference in orientation between P and R molecules on the one hand, and Q and S molecules on the other, the VIth order would be quite absent together with the IInd order, *i. e.* (100) would be quartered. However, as has already been stated, there is a difference in orientation, caused by a rotation about a tetragonal axis, and this difference will, in general, have its greatest effect on the reflexions of the prism-planes. It will be of less importance for the (101) plane, which makes, on account of the small axial ratio, an angle of only 28° 9′ with (001), and actually for this plane the agreement between calculated and observed intensities proves to be better for the higher orders. With regard to the (001) plane itself, P, Q, R, and S molecules are identical : the plane is really quartered.

The distribution of the molecules with regard to the (101) plane can be found by substituting the values of the co-ordinates of the 8 equivalent points in the equation of a plane :

$$hx+ky+lz=p,$$

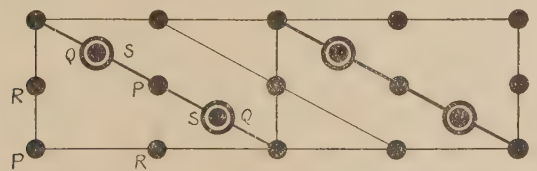
in which x, y, z are the coordinates of one of its points, expressed in fractions of the edges of the unit-cell, and h, k, l the indices of the plane *. When this is done for the 8 centres, p takes the values :

(*a*) $0, 0, 1, \frac{1}{2}, 1, 1, 1\frac{1}{2}, 1.$

In case *b* we get :

(*b*) $0, \frac{3}{4}-2u, 1\frac{1}{4}, 1-2u, \frac{1}{4}, -2u, 1, \frac{3}{4}-2u.$

Fig. 7.



a implies that the centres of the centro-symmetric molecules are located in two sets of (101) planes, the one set interleaving half-way the other set, and the planes contain alternately numbers of molecules in the ratio 6 : 2. This can also be seen in fig. 7, which represents a projection of the

* *Cf.* W. T. Astbury, "The Crystalline Structure of Anhydrous Racemic Acid," Proc. Roy. Soc. A, civ. p. 224.

unit-cell on a (100) plane. If again we consider the molecules as single scattering-centres, we can get a rough approximation of the intensities of the different orders of reflexion for the (101) plane by using the formula *

$$J \sim A^2 \frac{1+\cos^2 2\theta}{n^2},$$

in which θ and n have their usual meaning and A is the amplitude of the scattered rays. A is proportional to $(6-2)$ in the odd orders, and to $(6+2)$ in the even orders. The angle θ for the Ist order is 3° 22′.

Substituting these values, we get :

$$J_1 \sim \frac{(6-2)^2}{1^2} \times 1{\cdot}99, \quad i.e. \quad J_1 \sim 32,$$

$$J_2 \sim \frac{(6+2)^2}{2^2} \times 1{\cdot}95, \quad i.e. \quad J_2 \sim 31,$$

$$J_3 \sim \frac{(6-2)^2}{3^2} \times 1{\cdot}88, \quad i.e. \quad J_3 \sim 3{\cdot}3,$$

$$J_4 \sim \frac{(6+2)^2}{4^2} \times 1{\cdot}80, \quad i.e. \quad J_4 \sim 7{\cdot}2.$$

These numbers are in general agreement with the figures in the table, in so far that the Ist and IInd order are strong, compared with the very weak IIIrd order, and that the IVth order is stronger than the IIIrd.

In case *b* we have to take into consideration the different values of u; it is, however, easy to see that, assuming the same simplifications as before, for all values of u a weak IInd order for (101) would be expected. From the series

$$0, \tfrac{1}{4}\,;\ 1, 1\tfrac{1}{4}\,;\ -2u, \tfrac{3}{4}-2u\,;\ 1-2u, \tfrac{3}{4}-2u,$$

we see that for every molecule lying in a given (101) plane there is always a corresponding molecule lying in a plane removed from it by a distance $\frac{1}{4}d_{(101)}$; *i.e.* the rays reflected by any two such corresponding molecules are opposite in phase, and the IInd order is weak, in striking contrast with the experimental value, which shows the IInd order to be the strongest.

A consideration of the habit of the crystal is of importance because the best faces developed are generally the most closely packed with molecules †. According to Groth, crys-

* *Cf.* R. W. G. Wyckoff, 'The Structure of Crystals,' p. 102 (1924); also Sir W. H. Bragg and W. L. Bragg, 'X-rays and Crystal Structure,' pp. 114, 131, 206.

† *Cf.* W. T. Astbury, *l. c.* p. 225.

tals of i-erythritol show the following faces:—(100), (111), (131), (311). It is further stated that, besides (100), sometimes (111) is very large, sometimes (131). In the Davy-Faraday laboratory are splendid crystals of this substance, some of them measuring several *inches* across. They showed the same faces as given by Groth. (100), (111), and (131) were mostly very large, especially the first two; (311) was usually smaller. But besides these faces (110) was often present, always, however, very much smaller than (100). A few crystals showed (331) as a very small face. No other faces were found on these crystals.

Transforming the indices of these six planes, viz. (100), (111), (131) and (311), (110), (331), (face-centred cell) to the indices required of the body-centred cell which we have chosen, we obtain:

(110), (101), (211) and (121), (100), (301).

The numbers of molecules per unit-surface (σ) for different planes can be compared by determining for each plane the distance d_1 between successive planes which are equally packed with molecules. Indeed, $\frac{\sigma}{d_1}$ represents the number of molecules per unit-volume *, and is therefore a constant for the crystal. So we see that σ is proportional to d_1, and we can compare the molecular densities of different faces by comparing the spacings of equally packed planes parallel to them.

The spacings d_1 are either equal to the true spacings d (which are the distances between planes identical both with regard to the number of molecules as to the orientation of these molecules) or a sub-multiple of them.

The sub-multiple for each plane is found by substituting the coordinates of the eight equivalent points in the equation $hx+ky+lz=p$ of the plane, as has already been done for (101). We find in case *a* (centro-symmetrical molecules) that the planes which correspond to the true periodicity are interleaved by one or three parallel planes, also carrying molecules. Thus in those cases where successive planes are equally packed with molecules, the sub-multiple is clearly $\frac{1}{2}$ or $\frac{1}{4}$.

However, there are faces, *e. g.* (101), successive planes of which carry numbers of molecules in the ratio 3 : 1. With regard to these faces, equally packed planes have the true spacing d, but, the number of molecules in one series of

* See *e. g.*, P. P. Ewald, 'Kristalle und Röntgenstrahlen,' p. 26.

them being $\frac{3}{4}$ of all the molecules, the molecular-density σ is measured by $\frac{3}{4}$ of the spacing d.

In Table IV. a number of planes are tabulated according to decreasing spacings d (true spacing). The first column gives the indices of the planes (as used in our description), the second column d.

TABLE IV.

Plane.	d.	Centro-sym. molecules.		Axially-sym. molecules.	
		Sub-multiple number.	d_1.	Sub-multiple number.	d_1.
(100)	12·76	4	3·19	2	6·38
(110)	9·02	2	4·51	2	4·51
(001)	6·83	4	1·71	8	0·86
(101)	6·02	2*	4·51	4	1·50
(210)	5·72	4	1·43	2	2·86
(111)	5·44	4	1·36	8	0·68
(201)	4·66	4	1·17	8	0·58
(121)	4·38	2*	3·28	4	1·10
(310)	4·00	2	2·00	2	2·00
(221)	3·76	4	0·94	8	0·47
(301)	3·61	2*	2·71	4	0·90
(320)	3·54	4	0·89	2	1·77
(311)	3·47	4	0·87	8	0·43
(102)	3·30	4	0·82	4	0·82
(112)	3·19	2	1·59	2	1·59
(321)	3·14	2*	2·36	4	0·78
(410)	3·10	4	0·77	2	1·55
(122)	2·93	4	0·73	4	0·73

The third and fourth column refer to case *a*.

The numbers in the third column (sub-multiple numbers) indicate that the true spacings for the planes in question are "halved" or "quartered" by equally packed parallel planes; 2* indicates the special case mentioned, when the ratio of the numbers of molecules for successive planes is 3 : 1. The fourth column contains the "reduced" spacings d_1. The numbers in this column are proportional to the molecular-densities of the respective planes. When we arrange these numbers in order of magnitude, we obtain :

4·51 ; 4·51 ; 3·28 ; 3·19 ; 2·71 ; and so on,

corresponding to the faces :

(110), (101), (121) and (211), (100), (301), etc.

These are just the faces shown by the crystals.

A similar calculation can be made for case *b*. In the fifth and sixth columns of Table IV. are given the sub-multiple numbers and the "reduced" spacing d_1, calculated when no

special value is chosen for u. The agreement between the numbers d_1 and the actual faces of the crystal, which was obtained in case *a*, is in no way present in this case. It is possible by giving special values to u, e. g. $\frac{1}{8}$, to increase d_1 for several planes, but this does not influence the prism-planes. For all values of u (100) is closer packed than (110), while the crystal shows always (110) as a far better developed plane than (100). Likewise for all values of u (100) is closer packed than (101), and (210) closer packed than (121) ; the face (210) was not present on any of the crystals.

So the habit of the crystal is in perfect agreement with the hypothesis of centro-symmetric crystal-molecules of *i*-erythritol. The fact that there is often a difference in the development of the two faces (211) and (121) must be caused by the difference in orientation of the molecules with regard to these two planes, because the density of molecule-centres is the same for both. It was also observed that there was a marked difference between the reflexions from these two planes. The plane which has the stronger Ist order has the weaker IInd order.

Summary.

It is shown that the space-group of *i*-erythritol, which crystallizes in the tetragonal-bipyramidal class, is C_{4h}^{6}.

The body-centred unit-cell (Γ_t') contains eight molecules. The crystal-molecule must possess two-fold symmetry, either a centre or a two-fold axis. It is concluded that the crystal-molecule is centro-symmetrical, and the reasons are given on which this conclusion is based.

A crystallographic confirmation is thus given to the configuration of *i*-erythritol already assigned by stereochemistry.

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XXII. *On certain Functions of Two Variables and their Integrals related to the Bessel Coefficients.* *By* E. T. Bell *.

1. *The Functions* L.—Throughout the paper $n \geq 0$ is an integer; $\lambda, \mu, \nu, \rho, z, y$ are variables; and the ϵ_n are Neumann's factors, $\epsilon_0 = 1$, $\epsilon_{n+1} = 2$.

The function $L(\lambda, \mu)$ is defined by the absolutely convergent series for all finite λ, μ:

$$L_n(\lambda, \mu) = \tfrac{1}{2}n! \sum_0^\infty \frac{\lambda^{n+j}\mu^j}{j!\,(n+j)!}, \quad . \quad . \quad . \quad . \quad (1)$$

and we have

$$2L_n(\lambda, \mu) = n!\,\epsilon_n A_n(\lambda, \mu),$$

where

$$\exp(\lambda t + \mu t^{-1}) = A_0 + \sum_1^\infty (A_r t^r + B_r t^{-r}),$$

with

$$A_n \equiv A_n(\lambda, \mu), \quad B_n \equiv B_n(\lambda, \mu),$$

these being the functions of Spitzer †.

The introduction of the factor $\frac{1}{2}n!\,\epsilon$ in (1) is an essential modification. It greatly simplifies the algebraic details of the entire subject, and makes possible the use of an extremely simple symbolic method, explained in § 2, which otherwise is not practicable. The proofs of (20), (21) below illustrate as well as any others the gain in algebraic simplicity.

It follows from the definition (1), or immediately as in § 3, that

$$L_n(\lambda, -\mu) = \tfrac{1}{2}n!\,\epsilon_n(\sqrt{\lambda/\mu})^n J_n(2\sqrt{\lambda\mu}), \quad . \quad . \quad (2)$$

$$L_n\left(\frac{z}{2}, -\frac{z}{2}\right) = \tfrac{1}{2}n!\,\epsilon_n J_n(z), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $J_n(z)$ is the Bessel coefficient of order n. See also (12).

All of the information used here concerning $J_n(z)$ is available in chapter 2 of Watson's 'Theory of Bessel Functions' (1923) or in the 'Bessel Functions' of Gray, Mathews, and Macrobert (1922). From (2), (3) it follows that any formula for functions $L_u(\lambda, \mu)$ contains as a special case one for $J_n(z)$. The introduction of the factor $\frac{1}{2}n!\,\epsilon_n$

* Communicated by the Author.

† *Archiv für Math. u. Physik*, vol. iii. pp. 244–46 (1859).

thus enables us to apply the simple symbolic method to the Bessel coefficients. Many of the important integrals evaluated in terms of Bessel coefficients appear as degenerate forms (one variable equal to a constant) of integrals expressible as functions $L_n(\lambda, \mu)$. A short selection is given in §§ 8, 9.

2. *Umbral Notation.*—The *umbra* α is taken as the representative of the entire class of ordinary quantities, or *ordinaries*, α_n $(n=0, 1, \ldots)$, and α_n is written α until after the completion of all algebraic operations, when exponents are degraded to suffixes Umbral powers α^n, β^n are manipulated as if they were ordinaries; thus, for example,

$$\alpha^m . \alpha^n = \alpha^{m+n} = \alpha_{m+n}.$$

For z an ordinary, α an umbra, the umbral exponential function is

$$\exp \alpha z \equiv e^{\alpha z} \equiv \Sigma_0^\infty \alpha^n z^n/n! \equiv \Sigma \alpha_n z^n/n! ; \quad . \quad . \quad (4)$$

the umbral binomial theorem is

$$(\alpha+\beta)^n \equiv \Sigma_0^n \binom{n}{r} \alpha^{n-r}\beta^r \equiv \Sigma^n \binom{n}{r} \alpha_{n-r}\beta_r, \ (\alpha+\beta)^0 = \alpha_0\beta_0, \quad (5)$$

and hence

$$\exp \alpha z . \exp \beta z = \exp (\alpha+\beta)z . \quad . \quad . \quad . \quad (6)$$

The umbral or representative notation is due to Blissard.

3. *Expansions.*—The Laurent expansion of the left of (6.1) is valid for all $t \neq 0$. Assume that the expansion can be written in the form indicated, where ϕ^n, ψ^n are to be replaced by ϕ_n, ψ_n after expansion of the umbral exponentials,

$$\exp (\lambda t + \mu t^{-1}) = \exp \phi(\lambda, \mu)t + \exp \psi(\lambda, \mu)t^{-1}. \quad . \quad (6.1)$$

Replace t by t^{-1}; then

$$\phi(\lambda, \mu) = \psi(\mu, \lambda).$$

Compare with Spitzer's expansion in § 1 and (1); then

$$\exp (\lambda t + \mu t^{-1}) = \exp L(\lambda, \mu)t + \exp L(\mu, \lambda)t^{-1}. \quad . \quad (7)$$

From (7) and

$$\exp \tfrac{z}{2}(t - t^{-1}) = J_0(z) + \Sigma_1^\infty \{t^r + (-1)^r t^{-r}\} J_r(z)$$

we get (3), and from (7), with z, t replaced by $2\sqrt{\lambda\mu}, t\sqrt{\lambda/\mu}$ respectively, we see (2).

In (7) replace t by μt or by t/λ and compare with (7):

$$\mu^n \mathrm{L}_n(\lambda, \mu) = \lambda^n \mathrm{L}_n(\mu, \lambda) = \mathrm{L}_n(\lambda\mu, 1) = \mu^n \lambda^n \mathrm{L}_n(1, \mu\lambda), \quad (8)$$

and therefore (7) can be written

$$\exp(\lambda t + \mu t^{-1}) = \exp \mathrm{L}(\lambda, \mu) t + \exp \lambda^{-1}\mu \mathrm{L}(\lambda, \mu) t^{-1}, \quad (9)$$

or, what is the same,

$$\exp(\lambda t + \mu t^{-1}) = \Sigma_0^{\infty} \frac{\mathrm{L}_n(\lambda, \mu)}{n!} \left[t^n + \frac{\mu^n}{\lambda^n t^n} \right], \quad . \quad . \quad (10)$$

and hence by (2),

$$\exp(\lambda t - \mu t^{-1}) = \tfrac{1}{2}\Sigma\, \epsilon_n(\sqrt{\lambda/\mu})\mathrm{J}_n(2\sqrt{\lambda\mu})[t^n + (-\mu/\lambda)^n t^{-n}]. \quad (11)$$

In connexion with the integrals, the following, evident from (2) or (11), is important:

$$\mathrm{L}_n\left(\frac{y+z}{2}, \frac{y-z}{2}\right) = \frac{n!}{2} \epsilon_n \left(\sqrt{\frac{z+y}{z-y}}\right)^n \mathrm{J}_n(\sqrt{z^2 - y^2}). \quad (12)$$

4. *Derivatives.*—Write

$$\frac{\partial}{\partial\lambda} \mathrm{L}_n(\lambda, \mu) \equiv \mathrm{L}_{n\lambda}(\lambda, \mu) \equiv \mathrm{L}_\lambda{}^n(\lambda, \mu),$$

the last being umbral. The derivatives with respect to λ, μ of (7) upon reduction by (7) give at once

$$t[\exp \mathrm{L}(\lambda, \mu) t + \exp \mathrm{L}(\mu, \lambda) t^{-1}] = \exp \mathrm{L}_\lambda(\lambda, \mu) t + \exp \mathrm{L}_\lambda(\mu, \lambda) t^{-1},$$

$$t^{-1}[\exp \mathrm{L}(\lambda, \mu) t + \exp \mathrm{L}(\mu, \lambda) t^{-1}] = \exp \mathrm{L}_\mu(\lambda, \mu) t + \exp \mathrm{L}_\mu(\mu, \lambda) t^{-1}.$$

Equating coefficients of like powers of t, and observing (8), we get

$$\left.\begin{aligned}
\frac{\partial}{\partial\lambda} \mathrm{L}_0(\lambda, \mu) &= \frac{\mu}{2\lambda} \mathrm{L}_1(\lambda, \mu), \\
\frac{\partial}{\partial\mu} \mathrm{L}_0(\lambda, \mu) &= \tfrac{1}{2} \mathrm{L}_1(\lambda, \mu), \\
\frac{\partial}{\partial\lambda} \mathrm{L}_1(\lambda, \mu) &= 2\mathrm{L}_0(\lambda, \mu), \\
\frac{\partial}{\partial\mu} \mathrm{L}_{n+1}(\lambda, \mu) &= \frac{1}{n+2} \mathrm{L}_{n+2}(\lambda, \mu), \\
\frac{\partial}{\partial\lambda} \mathrm{L}_{n+2}(\lambda, \mu) &= (n+2) \mathrm{L}_{n+1}(\lambda, \mu).
\end{aligned}\right\} \quad . \quad . \quad (13)$$

These can be verified by (1).

5. *Recurrences.*—Write

$$L_n \equiv L_n(\lambda, \mu), \quad M_n \equiv L_n(\mu, \lambda).$$

Differentiate (7) with respect to t and get

$$[(\lambda - L)t^2 - \mu] \exp Lt + [\lambda t^2 - (\mu - M)] \exp Mt^{-1} = 0.$$

The result of equating to zero the several powers of t is

$$\mu L_2(\lambda, \mu) + 2L_1(\lambda, \mu) - 4\lambda L_0(\lambda, \mu) = 0, \quad . \quad . \quad (14)$$

$$\mu L_{n+3}(\lambda, \mu) + (n+3)(n+2)\,[L_{n+2}^{\prime}(\lambda, \mu) - \lambda L_{n+1}(\lambda, \mu)] = 0, \quad . \quad (15)$$

which enable us to compute the functions L_n successively from L_0, L_1. For $2\lambda = -2\mu = z$ these give as a check the recurrence for $J_n(z)$.

6. *Differential Equations.*—Write $y \equiv L_n(\lambda, \mu)$. Then an easy reduction by (13), (14), (15) gives immediately

$$\frac{\partial^2 y}{\partial \lambda \partial \mu} = y, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

$$\lambda \frac{\partial y}{\partial y} - \mu \frac{\partial y}{\partial \mu} = ny, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

and therefore by differentiation of (17),

$$\lambda \frac{\partial^2 y}{\partial \lambda^2} - (n-1)\frac{\partial y}{\partial \lambda} - \mu y = 0, \quad . \quad . \quad . \quad . \quad (18)$$

$$\mu \frac{\partial^2 y}{\partial \mu^2} + (n+1)\frac{\partial y}{\partial \mu} - \lambda y = 0, \quad . \quad . \quad . \quad . \quad (19)$$

the last two of which for $2\lambda = -2\mu = z$ reduce to Bessel's equation for $J_n(z)$.

7. *Addition Theorem.*—If α, β are any umbræ we have from (1) the definition, provided the series be convergent,

$$L_n(\alpha, \beta) \equiv \frac{n!}{2} \epsilon_n \Sigma_0^{\infty} \frac{\alpha_{n+j}\beta_j}{j!\,(n+j)!}.$$

By means of L functions whose arguments are umbræ, the addition theorem can be given the remarkably concise finite form :

$$L_n(\lambda + \nu, \mu + \rho) = [L(\lambda, \mu) + L(\nu, \rho)]^n + L_n[L(\lambda, \mu), L(\rho, \nu)] + L_n[L(\nu, \rho), L(\mu, \lambda)]. \quad (20)$$

The proof is immediate. In (7) replace λ, μ by ν, ρ respectively, multiply member by member the identity so

obtained by (7), use (6) to reduce the left, multiply out the product on the right, apply (6), (7) to the result, and equate coefficients of t^n.

Without the use of umbræ we have from (20),

$$\mathrm{L}_n(\lambda+\nu,\ \mu+\rho) = \Sigma_0^n \binom{n}{r} \mathrm{L}_{n-r}(\lambda,\ \mu)\mathrm{L}_r(\nu,\ \rho) + \frac{n!}{2}\epsilon_n \Sigma_0^\infty \frac{1}{j!\,(n+j)!}\left[\mathrm{L}_{n+j}(\lambda,\ \mu)\mathrm{L}_j(\rho,\ \nu) + \mathrm{L}_{n+j}(\nu,\ \rho)\mathrm{L}_j(\mu,\ \lambda)\right], \quad . \ . \ . \ . \ . \ . \ . \ . \ (21)$$

which by (3), with $2\lambda = -2\mu = z$, $2\nu = -2\rho = w$, gives the usual addition theorem for $\mathrm{J}_n(z+w)$. Neither J_n nor Spitzer's A_n has a finite (umbral) addition theorem like (20), owing to the lack of the factor $n!$

8. *Integrals.*— A great variety of integrals can be evaluated by means of the L functions ; a few illustrations must suffice here. In (10) replace t by $\exp i\theta$, equate reals and imaginaries in the result, and put $\lambda+\mu=y$, $\lambda-\mu=z$:

$$e^{y\cos\theta}\cos(z\sin\theta) = \Sigma_0^\infty \left[1+\left(\frac{y-z}{y+z}\right)^n\right] \mathrm{L}_n\left(\frac{y+z}{2},\ \frac{y-z}{2}\right)\frac{\cos n\theta}{n!}, \quad (22)$$

$$e^{y\sin\theta}\sin(z\sin\theta) = \Sigma_0^\infty \left[1-\left(\frac{y-z}{y+z}\right)^n\right] \mathrm{L}_n\left(\frac{y+z}{2},\ \frac{y-z}{2}\right)\frac{\sin n\theta}{n!}. \quad (23)$$

To express these in terms of Bessel coefficients, we write

$$\tfrac{1}{2}\epsilon_n\left[\left(\frac{z+y}{z-y}\right)^{n/2}+(-1)^n\left(\frac{z-y}{z+y}\right)^{n/2}\right]\mathrm{J}_n\left(\sqrt{z^2-y^2}\right) \equiv \mathrm{R}_n(y,\ z),$$

$$\tfrac{1}{2}\epsilon_n\left[\left(\frac{z+y}{z-y}\right)^{n/2}-(-1)^n\left(\frac{z-y}{z+y}\right)^{n/2}\right]\mathrm{J}_n\left(\sqrt{z^2-y^2}\right) \equiv \mathrm{S}_n(y,\ z),$$

and refer to (12), whence

$$e^{y\cos\theta}\cos(z\sin\theta) = \Sigma_0^\infty \mathrm{R}_n(y,\ z)\cos n\theta, \quad . \quad (24)$$

$$e^{y\cos\theta}\sin(z\sin\theta) = \Sigma_0^\infty \mathrm{S}_n(y,\ z)\sin n\theta. \quad . \quad (25)$$

Henceforth a summation without indicated limits refers to $n=0$ to ∞, and we shall write when convenient

$$\mathrm{R}_n(y,\ z) \equiv \mathrm{R}_n, \quad \mathrm{S}_n(y,\ z) \equiv \mathrm{S}_n.$$

Multiply (24), (25) throughout by $\cos n\theta$, $\sin n\theta$ respectively, and integrate from 0 to π :

$$\epsilon_n \int_0^\pi e^{y\cos\theta} \cos(z\sin\theta)\cos n\theta\, d\theta = \pi \mathrm{R}_n, \quad . \quad . \quad (26)$$

$$2\int_0^\pi e^{y\cos\theta} \sin(z\sin\theta)\sin n\theta\, d\theta = \pi \mathrm{S}_n, \quad . \quad . \quad (27)$$

and therefore by addition and subtraction,

$$2\epsilon_n \int_0^\pi e^{y\cos\theta} \cos(z\sin\mp n\theta)\, d\theta = \pi(2\mathrm{R}_n \pm \epsilon_n \mathrm{S}_n). \quad (28)$$

For $n=0$ this becomes Parseval's integral,

$$\int_0^\pi e^{y\cos\theta} \cos(z\sin\theta)\, d\theta = \pi \mathrm{J}_0(\sqrt{z^2-y^2}) ; \quad (28.1)$$

while for $r>0$ (28) gives

$$\int_0^\pi e^{y\cos\theta} \cos(z\sin-r\theta)\, d\theta = \pi\left(\frac{z-y}{z+y}\right)^{r/2} \mathrm{J}_r(\sqrt{z^2-y^2}),$$
$$. \quad . \quad . \quad (28.2)$$

which for $y=0$ is Bessel's integral, and

$$\int_0^\pi e^{y\cos\theta} \cos(z\sin+r\theta)\, d\theta = (-1)^r \pi\left(\frac{z-y}{z+y}\right)^{r/2} \mathrm{J}_r(\sqrt{z^2-y^2}).$$
$$. \quad . \quad . \quad (28.3)$$

Take the rth derivatives ($r>0$) with respect to y, z of (26), (27) :

$$\epsilon_n \int_0^\pi e^{y\cos\theta} \cos(z\sin\theta)\cos n\theta \cos^r\theta\, d\theta = \pi \partial^r \mathrm{R}_n/\partial y^r, \quad . \quad . \quad . \quad . \quad (26.1)$$

$$2\int_0^\pi e^{y\cos\theta} \sin(z\sin\theta)\sin n\theta \cos^r\theta\, d\theta = \pi \partial^r \mathrm{S}_n/\partial y^r, \quad . \quad . \quad . \quad . \quad (27.1)$$

$$\epsilon_n \int_0^\pi e^{y\cos\theta} \cos(z\sin\theta)\cos n\theta \sin^{2r}\theta\, d\theta = (-1)^r \pi \partial^{2r} \mathrm{R}_n/\partial z^{2r}, \quad . \quad . \quad (26.2)$$

$$2\int_0^\pi e^{y\cos\theta} \sin(z\sin\theta)\sin n\theta \sin^{2r}\theta\, d\theta = (-1)^r \pi \partial^{2r} \mathrm{S}_n/\partial z^{2r}, \quad . \quad . \quad (27.2)$$

$$\epsilon_n \int_0^\pi e^{y\cos\theta} \sin(z\sin\theta)\cos n\theta \sin^{2r-1}\theta\, d\theta = (-1)^r \pi \partial^{2r-1} \mathrm{R}_n/\partial z^{2r-1}, \quad (26.3)$$

$$2\int_0^\pi e^{y\cos\theta} \cos(z\sin\theta)\sin n\theta \sin^{2r-1}\theta\, d\theta = -(-1)^r \pi \partial^{2r-1} \mathrm{S}_n/\partial z^{2r-1}. \quad (27.3)$$

In (26.2), (26.3) take $y=n=0$:

$$\int_0^\pi \cos(z\sin\theta)\sin^{2r}\theta\,d\theta = (-1)^r\pi d^{2r}\mathrm{J}_0(z)/dz^{2r}, \quad (28)$$

$$\int_0^\pi \sin(z\sin\theta)\sin^{2r-1}\theta\,d\theta = (-1)^r\pi d^{2r-1}\mathrm{J}_0(z)/dz^{2r-1}, \quad (29)$$

the first of which gives Poisson's integral. If in (24), (25) we increase θ by $s\pi/2$ $(s=1, 2, 3)$ we get three further sets of integrals in a similar way.

If in (24), (25) we change y into $-y$, add or subtract the new results and the old, and proceed as above, we obtain integrals such as

$$\int_0^\pi \cosh(y\cos\theta)\cos(z\sin\theta)\,d\theta$$

expressed at once in terms of Bessel's coefficients. As before, θ may be replaced by $\theta+s\pi/2$, giving a new chain of integrals. Omitting all these we pass to the type

$$\int_0^\pi f(y\,\phi(\theta))g(z\,\psi(\theta))d\theta,$$

where each of f, ϕ, g, ψ is any one of sin, cos.

9. In the definitions of R_n, S_n replace y by iy and separate reals and imaginaries,

$$\mathrm{R}_{2n}(iy, z) = \mathrm{T}_{2n}(y, z), \quad \mathrm{S}_{2n+1}(iy, z) = \mathrm{T}_{2n+1}(y, z),$$

both of which are real, and

$$\mathrm{S}_{2n}(iy, z) = i\mathrm{U}_{2n}(y, z), \quad \mathrm{R}_{2n+1}(iy, z) = i\mathrm{U}_{2n+1}(y, z),$$

both of which are pure imaginary, where the functions T_n, U_n are defined by

$$\mathrm{T}_n(y, z) \equiv \mathrm{T}_n \equiv \epsilon_n\mathrm{J}_n(\sqrt{z^2+y^2})\left[\frac{(z+iy)^n+(z-iy)^n}{2(\sqrt{z^2+y^2})^n}\right],$$

$$\mathrm{U}_n(y, z) \equiv \mathrm{U}_n \equiv \epsilon_n\mathrm{J}_n(\sqrt{z^2+y^2})\left[\frac{(z+iy)^n-(z-iy)^n}{2i(\sqrt{z^2+y^2})^n}\right].$$

Hence, replacing y by iy in (24) we get

$$\cos(y\cos\theta)\cos(z\sin\theta) = \Sigma\,\mathrm{T}_{2n}\cos 2n\theta, \quad (30)$$

$$\sin(y\cos\theta)\cos(z\sin\theta) = \Sigma\,\mathrm{U}_{2n+1}\cos(2n+1)\theta, \quad (31)$$

and similarly from (25),

$$\cos(y\cos\theta)\sin(z\sin\theta) = \Sigma\,\mathrm{T}_{2n+1}\sin(2n+1)\theta, \quad (32)$$

$$\sin(y\cos\theta)\sin(z\sin\theta) = \Sigma\,\mathrm{U}\quad\sin 2n\theta. \quad (33)$$

We shall omit the complete set of similar expansions obtainable by successive increases of θ by $\pi/2$. The following generalizations of two results due to Jacobi are of interest. By additions and subtractions of (30)–(33) we have

$$\cos(y\cos\theta \pm z\sin\theta) = \Sigma\,(T_{2n}\cos 2n\theta \mp U_{2n}\sin 2n\theta), \quad (34)$$

$$\sin(y\cos\theta \pm z\sin\theta) = \Sigma\,[U_{2n+1}\cos(2n+1)\theta \pm T_{2n+1}\sin(2n+1)\theta], \quad (35)$$

which for y or $z=0$ become the results in question, as also do (30), (31) for $z=0$, and (32) $y=0$. If in the definitions of T_n, U_n we put $z=w\cos\phi$, $y=w\sin\phi$, we get from (30)–(33):

$$\cos(w\sin\phi\cos\theta)\cos(w\cos\phi\sin\theta) = \Sigma\,\epsilon_{2n}J_{2n}(w)\cos 2n\phi\cos 2n\theta, \quad (36)$$

$$\sin(w\sin\phi\cos\theta)\cos(w\cos\phi\sin\theta) = \Sigma\,J_{2n+1}(w)\sin(2n+1)\phi\cos(2n+1)\theta, \quad (37)$$

$$\cos(w\sin\phi\cos\theta)\sin(w\cos\phi\sin\theta) = \Sigma\,J_{2n+1}(w)\cos(2n+1)\phi\sin(2n+1)\theta, \quad (38)$$

$$\sin(w\sin\phi\cos\theta)\sin(w\cos\phi\sin\theta) = \Sigma\,\epsilon_{2n}J_{2n}(w)\sin 2n\phi\sin 2n\theta, \quad (39)$$

which, however, can be obtained from the corresponding modifications of (34), (35) by additions and subtractions, and these in turn follow at once from Jacobi's expansions by putting therein $\phi \pm \theta$ for θ. Multiply (30) throughout by $\cos 2n\theta$ and integrate from 0 to π,

$$\epsilon_{2n}\int_0^\pi \cos(y\cos\theta)\cos(z\sin\theta)\cos 2n\theta\,d\theta = \pi T_{2n}, \quad (40)$$

and similarly from (31)

$$2\int_0^\pi \sin(y\cos\theta)\cos(z\sin\theta)\cos(2n+1)\theta\,d\theta = \pi U_{2n+1}, \quad (41)$$

while from (32), (33) we get

$$2\int_0^\pi \cos(y\cos\theta)\sin(z\sin\theta)\sin(2n+1)\theta\,d\theta = \pi T_{2n+1}, \quad (42)$$

$$2\int_0^\pi \sin(y\cos\theta)\sin(z\sin\theta)\sin 2n\theta\,d\theta = \pi U_{2n}. \quad (43)$$

From (36)–(39) we have several double integrals for $J_n(z)$, of which the following is one:

$$\epsilon_{2n}\int_0^{\pi}\int_0^{\pi}\cos(w\sin\phi\sin\theta)\cos(w\cos\phi\sin\theta)\cos 2n\theta \cos 2n\phi\, d\theta\, d\phi = \pi^2 J_{2n}(w). \quad (44)$$

As before, by differentiations and changes of the argument, the integrals already indicated furnish many more. If we multiply together the Fourier series for $\cos(y\cos\theta)$, $\cos(z\sin\theta)$, which can be written down from (32) by putting $z=0$, $y=0$ in turn, and equate the coefficient of $\cos 2n\theta$ to T_{2n}, we arrive at the expression of $J_n(\sqrt{z^2+y^2})$ in terms of Bessel coefficients having the respective arguments z, y. Many other such theorems are sufficiently suggested by the expansions. Thus, the functions of y, z and the identities between them obtained by equating coefficients of like powers of $\sin\theta$ or $\cos\theta$ in (30) and other expansions of the same type, are of interest. These are the analogues of the expansions of powers of a single variable in a series of Bessel coefficients.

Finally, a great number of summations involving Bessel coefficients can be effected by multiplying any of the expansions such as (24), (25), (30)–(39) by a power of $\sin x$ or of $\cos x$ and integrating between the limits 0, π.

XXIII. *The X-Ray Spectra of the Lower Elements.* *By* Robert Thoræus *.

[Plate IV.]

Part I.

In two previous papers †, Prof. M. Siegbahn and the author have given the preliminary results of some attempts to extend the range of registered wave-lengths within the K- and L-Series. This work was found to be attended by many difficulties, among which especially may be mentioned the absorption of this weak radiation. These difficulties,

* Communicated by Prof. Manne Siegbahn. An abstract of this paper, entitled "Extension of the Range of X-Ray Spectra against Longer Wave-lengths," and containing the wave-lengths and a short description of the high-vacuum spectrograph, was read before a meeting of Danish, Norwegian, and Swedish physicists at Oslo, August 25th, 1925.

† *Arkiv f. Mat., Astr. och Fys.* Bd. xviii. No. 24 (1924); Bd. xix. A. No. 12 (1925).

however, were fairly successfully overcome by building a high-vacuum spectrograph that has been found to be very good for this purpose, and so it has also been used during the present investigation.

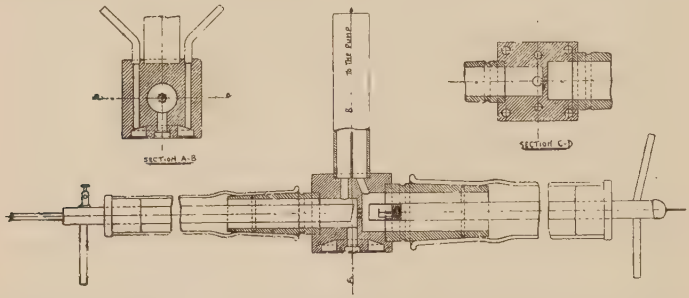
Among the earlier known crystals, gypsum, mica, and sugar are the only ones that can be used for reflecting those long wave-lengths. The upper limit being about 18 Å.U., they cannot be used for the whole range of wave-lengths investigated here. There are, however, many organic compounds suitable for this purpose. Especially lauric acid and palmitic acid have proved to be good. Their reflecting power is good, and their melting-points so high that they practically do not evaporate in vacuum. In the two papers mentioned above the lattice constant of palmitic acid and some wave-lengths were given. Those values are now checked and together with some new ones given with the best accuracy available within this range of wave-lengths. By other authors it has earlier been pointed out that the X-ray lines become broader and diffuse when the wave-lengths increase. This also appears here. For instance, when taking Cu Lα by means of gypsum and a slit of 0·2 mm. width, I get a line 2·5 mm. wide. Because of this it is rather difficult to give very exact values of the long wave-lengths. In order to get the measurements as uniform as possible I have, however, measured all the lines to their maximum of blackening.

The general arrangement of the apparatus has already been published *. In connexion with this investigation, however, two new types of X-ray tube have been built and tested. When wolfram filaments are used, a thin deposit of metallic wolfram is always to be found on the emission-surface of the anticathode, and in this deposit a strong absorption of the radiation of long wave-lengths will appear. To prevent this absorption a thin metallic foil may be inserted between the cathode and the anticathode. When the electrons pass through this foil their speed will be decreased, but this difficulty can easily be overcome by increasing the tension. Fig. 1 gives the general arrangement of a tube built on this principle. The body of the tube and the cathode and anticathode are of standard make. In the middle of the tube a metallic wall is arranged and fitted with a number of small holes, the diameters of which are about 1 mm. By covering the wall on the anticathode side with a thin aluminium foil (5–7μ) the above deposit is

* *Arkiv f. Mat., Astr. och Fys.* Bd. xix. A, No. 12 (1925).

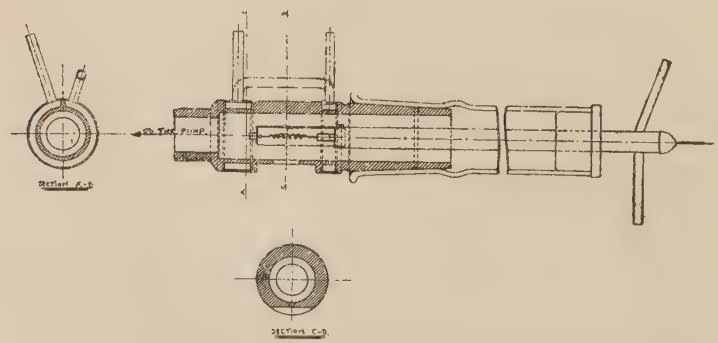
quite eliminated. Moreover, as the window of the X-ray tube is taken away, this arrangement will also protect the photographic plate from fogging by the ordinary light from the hot filament. To get a good cooling of the foil the wall should be rather thick (2–3 mm.), otherwise it would immediately melt because of the heat from the hot filament and the energy that the electrons lose when passing through the foil. The tube itself as well as the cathode and

Fig. 1.



anticathode are supplied with an efficient water-cooling system. Both the cathode and the anticathode are connected to the tube by glass-grindings, thus allowing the tube to be kept working with either one terminal earthed or both of them high-tensioned. For evacuating the tube two channels are arranged, both of them debouching into a wider tube that is connected to the pump. By this arrangement the light from the hot filament cannot come inside the spectrograph and blacken the photographic plate.

Fig. 2.



In fig. 2 the other type of X-ray tube is to be seen. Only the cathode is here standard made. The body of the

tube is cylindrical and supplied with a longitudinal slit the size of which is 15×2 mm. The slit is covered by a metallic foil (10μ) soldered to the body of the tube and acting as anticathode, on which the different substances may be placed when their radiation is to be examined. Other details will easily be understood from the drawing.

Both the types have proved to be rather good, especially when working with X-ray spectra of long wave-lengths.

The spectrograms were taken on film strips placed in a circular bent holder and at a distance of 135·70 mm. from the reflecting surface of the crystal.

All the wave-lengths given below are based upon the wave-length of the Na Kα line. Hjalmar*, in his precision measurements, has found the value Na K$\alpha\,\lambda = 11{\cdot}884$ Å.U. Assuming this value to be right and always working with spectra of the 1st order, the measurements have proceeded in the following way.

The Lα and Lβ lines of Zn(30) and Cu(29) were determined to Na Kα as reference and by means of a gypsum crystal, the lattice constant of which is

$$d = 7{\cdot}578 \text{ Å.U.} \quad \text{and} \quad \log 2d = 1{\cdot}18056.$$

From the plates T. 179 and 181 were calculated

$$\text{Zn} \begin{cases} \text{L}\alpha = 12{\cdot}224 \text{ Å.U.} \\ \text{L}\beta = 11{\cdot}958 \text{ Å.U.} \end{cases} \quad \text{and} \quad \text{Cu} \begin{cases} \text{L}\alpha = 13{\cdot}308 \text{ Å.U.} \\ \text{L}\beta = 13{\cdot}029 \text{ Å.U.} \end{cases}$$

Then the Lα and Lβ lines of Ni(28) and Co(27) were determined to Zn Lα as reference and by using a mica crystal, the lattice constant of which is

$$d = 9{\cdot}927 \text{ A.U.} \quad \text{and} \quad \log 2d = 1{\cdot}29786.$$

This value belongs to reflexion in the 1st order, and is taken from an investigation in this laboratory by Mr. Axel Larsson†. From the plates T. 183 and 184 were calculated

$$\text{Ni} \begin{cases} \text{L}\alpha = 14{\cdot}528 \text{ Å.U.} \\ \text{L}\beta = 14{\cdot}235 \text{ Å.U.} \end{cases} \quad \text{and} \quad \text{Co} \begin{cases} \text{L}\alpha = 15{\cdot}940 \text{ Å.U.} \\ \text{L}\beta = 15{\cdot}62 \text{ Å.U.} \end{cases}$$

In order to get the lattice constants of lauric acid and palmitic acid, the Lα lines of Zn(30), Cu(29), Ni(28), and Co(27) were taken as symmetrical double registerings. The following Tables I. and II. give the calculated angles.

* Phil. Mag. vol. xli. April 1921.

† *Arkiv f. Mat., Astr. och Fys.* Bd. xix. A, No. 14 (1925).

TABLE I.

Lauric acid.

Plate No.	Line.	Distance mm.	Angle ϕ.
186..	Zn Lα	89·3	12° 56′·9
187.....	Cu Lα	97·4	14° 7′·4
188.....	Ni Lα	106 6	15° 27′·4
189.....	Co Lα	117·2	16° 59′·6

Note.—The measured distances in this table refer to 98·6 mm. distance between the crystal and the plate-holder.

TABLE II.

Palmitic acid.

Plate No.	Line.	Distance mm.	Angle ϕ.
198.....	Zn Lα	94·0	9° 55′·0
193.....	Cu Lα	102·3	10° 47′·6
194.....	Ni Lα	112·0	11° 49′·0
195	Co Lα	123 2	12° 59′·9

Inserting these angles and the above given wave-lengths corresponding to them in the Bragg formula, we get the following values of the lattice constants :—

Lauric acid :

From Zn Lα : $\log 2d = 1{\cdot}73683$
Cu Lα : $\log 2d = 1{\cdot}73670$
Ni Lα : $\log 2d = 1{\cdot}73650$
Co Lα : $\log 2d = 1{\cdot}73672$

Mean value : $\log 2d = 1{\cdot}73669$ and $2d = 54{\cdot}536$ Å.U.

Palmitic acid :

From Zn Lα : $\log 2d = 1{\cdot}85113$
Cu Lα : $\log 2d = 1{\cdot}85167$
Ni Lα : $\log 2d = 1{\cdot}85098$
Co Lα : $\log 2d = 1{\cdot}85084$

Mean value : $\log 2d = 1{\cdot}85116$ and $2d = 70{\cdot}98$ Å.U.

Then the Lα and Lβ lines of Fe (26) and the Kα line of F (9) were taken as symmetrical double registerings by means of palmitic acid, and the plates calculated with the above value of the lattice constant. From the plates T. 196 and 197 the following values are obtained :—

$$\text{Fe}\begin{cases} \text{L}\alpha: d=135{\cdot}9 \text{ mm.}, & \phi=14^\circ\ 20'{\cdot}2, & \lambda=17{\cdot}58 \text{ Å.U.} \\ \text{L}\beta: d=133{\cdot}1 \text{ mm.}, & \phi=14^\circ\ 2'{\cdot}5, & \lambda=17{\cdot}22 \text{ Å.U.} \end{cases}$$

$$\text{F}\quad \text{K}\alpha: d=141{\cdot}3 \text{ mm.}, \quad \phi=14^\circ\ 56'{\cdot}4, \quad \lambda=18{\cdot}30 \text{ Å.U.}$$

Using the palmitic acid as crystal, the L-Series of Mn (25) and Cr (24) were taken to Cu Lα as reference. The plates T. 202 and 215 belong to these exposures and give the following results :—

$$\text{Mn}\begin{cases} \text{L}\alpha: \phi=15^\circ\ 51'{\cdot}4, & \lambda=19{\cdot}39 \text{ Å.U.} \\ \text{L}\beta: \phi=15^\circ\ 33'{\cdot}7, & \lambda=19{\cdot}04 \text{ Å.U.} \end{cases}$$

$$\text{Cr}\begin{cases} \text{L}\alpha: \phi=17^\circ\ 39'{\cdot}1, & \lambda=21{\cdot}53 \text{ Å.U.} \\ \text{L}\beta: \phi=17^\circ\ 22'{\cdot}0, & \lambda=21{\cdot}19 \text{ Å.U.} \end{cases}$$

Within the L-Series it has also been possible to measure the weaker doublet $l\eta$. For taking this doublet palmitic acid has been used for the elements below 31, and gypsum or mica for those ones above 32. From the following Table III. are to be seen the substances applied to the anticathode, and in Table IV. all the wave-lengths are collected.

Table III.

Element No.	Substance applied.	Way of application.
35 Br	NaBr (powder).	The copper anticathode was scratched with a knife and the powder pressed into the scratches.
34 Se	Se (powder).	
33 As	As (powder).	
30 Zn	Metallic plate.	The metallic plates were dove-tailed into the emitting surface of the anticathode.
29 Cu	Pure anticathode.	
28 Ni	Metallic plate.	
27 Co	„ „	
26 Fe	„ „	
25 Mn	Electrolytic deposit on copper plates.	
24 Cr		
9 F	NaF (powder).	As the above powders.

TABLE IV. *a*

Element No.	Lℓ.			Lη.			$L\alpha_1\,\alpha_2$.			Lβ1.		
	λ Å.U.	ν/R.	$\sqrt{\nu/R}$.	λ Å.U.	ν/R.	$\sqrt{\nu/R}$.	λ Å.U.	ν/R.	$\sqrt{\nu/R}$.	λ Å.U.	ν/R.	$\sqrt{\nu/R}$.
37 Rb	—	—	—	8·029[1]	113·50	10·653	7·303[1]	124·79	11·171	7·060[1]	129·07	11·361
35 Br	9·563	95·29	9·762	9·234	98·68	9·934	8·357[1]	109·05	10·442	8·108[1]	112·40	10·602
34 Se	10·271	88·72	9·419	9·939	91·69	9·576	8·971[1]	101·58	10·079	8·717[1]	104·54	10·225
33 As	11·047	82·50	9·083	10·710	85·08	9·224	9·650[1]	94·43	9·718	9·394[1]	97·01	9·850
30 Zn	13·95	65·33	8·082	13·61	66·96	8·183	12·224	74·55	8·634	11·958	76·21	8·730
29 Cu	15·19	59·99	7·746	14·83	61·45	7·839	13·308	68·48	8·275	13·029	69·97	8·365
28 Ni	16·55	55·06	7·421	16·17	56·36	7·507	14·528	62·72	7·920	14·235	64·02	8·001
27 Co	18·20	50·07	7·076	17·77	51·28	7·161	15·94	57·17	7·561	15·62	58·34	7·637
26 Fe	20·12	45·29	6·730	19·65	46·38	6·810	17·58	51·84	7·200	17·22	52·92	7·275
25 Mn	—	—	—	—	—	—	19·39	46·98	6·855	19·04	47·93	6·923
24 Cr	—	—	—	—	—	—	21·53	42·33	6·506	21·19	43·01	6·558

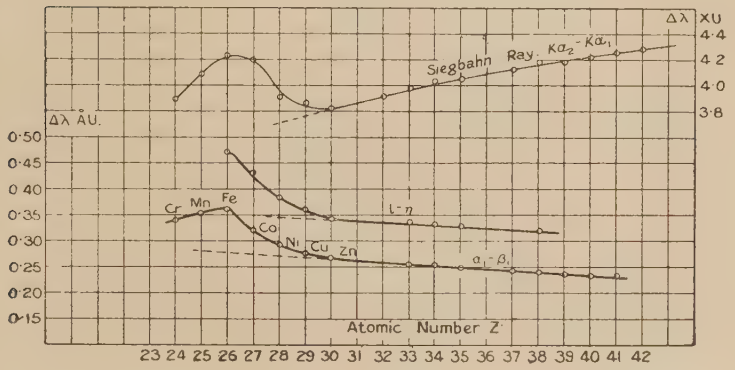
[1] Earlier measurements by other authors.

TABLE IV. *b*

Element No.	$K\alpha_1\,\alpha_2$.		
	λ Å.U.	ν/R.	$\sqrt{\nu/R}$.
9 F	18·30	49·80	7·057

By calculating the wave-length differences $L\alpha_1 - L\beta_1$ and $Ll - L\eta$, and plotting them against the atomic number Z we get the diagram in fig. 3. It is clearly to be seen, how the running of the curves suddenly changes at Cu, and how the values of the elements below Cu form something like a peak the top of which belongs to Fe (26). In an earlier paper Prof. M. Siegbahn and Mr. B. B. Ray * have studied the doublet-difference $K\alpha_1 - K\alpha_2$ within this range of elements, and found within the K-Series an effect of the

Fig. 3.



same appearance as the one in fig. 3. This is not a mere chance, but will be quite understood when looking at the energy-level diagram in fig. 4. As may be seen, all the lines $K\alpha_1$, $K\alpha_2$, $L\alpha_1$, $L\beta_1$, Ll, and $L\eta$ are formed by transitions. either *from* the levels L_{II} and L_{III} or *to* those ones. The small difference between the lines $L\alpha_1$ and $L\alpha_2$ is not taken into account, as the dispersion used here is not sufficient to separate them. In consequence of this it may be expected that for every element within this range the differences in ν/R of ($L\beta_1$–$L\alpha_2$), ($L\eta$–Ll), and ($K\alpha_1$–$K\alpha_2$) should be all the same. How far this is the case will be seen from the following Table V.

The differences $K\alpha_1 - K\alpha_2$ are calculated from the values in Siegbahn's book, 'The Spectroscopy of X-Rays.'

* *Arkiv f. Mat., Astr. och Fys.* Bd. xviii. No. 19 (1924).

Fig. 4.

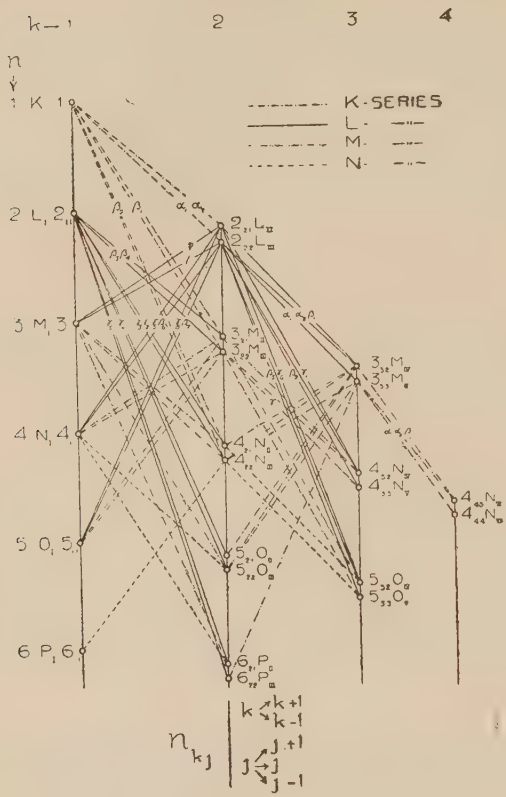


TABLE V.—Differences in ν/R.

Element No.	L-Series.		K-Series.
	$\beta_1-\alpha_1$.	$\eta-l$.	$\alpha_1-\alpha_2$.
37 Rb	4·28	—	4·38
35 Br	3·35	3·39	3·40
34 Se	2·96	2·97	2·99
33 As	2·58	2·58	2·62
30 Zn	1·66	1·63	1·71
29 Cu	1·49	1·46	1·42
28 Ni	1·30	1·30	1·33
27 Co	1·17	1·21	1·24
26 Fe	1·08	1·09	1 04
25Mn	0·95	—	—
24 Cr	0·68	—	0·72

In Plate IV. I have collected some photograms taken with palmitic acid during this investigation. The film-strips are arranged one above the other with their direct beam blackenings on a vertical.

Upsala, Physical Laboratory of the University.
September 29th, 1925.

XXIV. *On the Optical Properties of Chromatic Emulsions.* *By* C. M. Sogani, *M.Sc.*, *Assistant Professor of Physics, Benares Hindu University* *.

[Plate V.]

1. *Introduction.*

IT has long been known that emulsions exhibiting structural colour may be obtained by shaking up glycerine and turpentine, the phenomenon arising from the fact that the liquids have equal refractive indices for some particular part of the spectrum but not for others. These emulsions are, however, somewhat transient as the liquids speedily separate into distinct layers. Recently, Holmes and Cameron † have succeeded in preparing a considerable variety of coloured emulsions using a suitable emulsifying agent and choosing for the continuous phase a mixture whose refractive index may be continuously adjusted by varying its composition. The emulsions obtained in this way are fairly permanent and are exceedingly beautiful by reason of the play of colours which they exhibit. Qualitative studies of the optical effects exhibited by glycerine-turpentine emulsions were carried out some years ago at the suggestion of Prof. C. V. Raman by N. K. Sethi ‡. The present work was also undertaken at his instance to study the optical properties of the emulsions obtained with an emulsifying agent, the comparative permanence of which greatly facilitates the work and widens the range of investigation. The research undertaken included a study of the spectral range of the light transmitted by the emulsions, their refractivity, the character of the diffraction-haloes produced by them, their surface colours, and the influence of the dispersive powers of the liquid used, of the particle-size,

* Communicated by Prof. C. V. Raman, M.A., D.Sc., F.R.S.

† Am. Chem. Soc. Journ. xliv. pp. 71–74, Jan. 1922.

‡ N. K. Sethi, Proceedings of the Indian Assn. for the Cult. of Science, vol. vi. p. 134 (1920–21).

and of the depth of the emulsion on its optical behaviour. The paper sets out the results of work carried out on these points, together with a theoretical discussion. Probably the most interesting new phenomenon noticed in the course of the experiments is that the light scattered by an emulsion in which the disperse phase consists of droplets of uniform size closely packed together is concentrated in sharply-defined circular diffraction-rings, the effect being somewhat analogous to that obtained with monochromatic X-rays in the powder method of crystal analysis.

2. *Some Observations with Non-homogeneous Emulsions.*

We shall deal in this and the two following sections with emulsions containing particles of non-uniform size. The case of uniform particles will be considered later in the paper.

For the observations described below, some of the emulsions mentioned by Holmes and Cameron were prepared and used.

Spectrum of the Transmitted Light.—To determine the spectrum of the transmitted light, the image of a small source of white light was formed by means of a lens on the slit of a wave-length spectrometer placed 2 or 3 metres away from the source. The cell containing the emulsion was placed just in front of the lens (between it and the source). The spectral region of transmission obtained is always quite narrow. It is not, however, an invariable quantity, but is found to be dependent on a number of factors. To give an idea of the range of transmission, a particular case of the emulsion of glycerine in a mixture of benzene and acetone may be mentioned here. In this case, with a thickness of the emulsion of 3 cm. and a mean diameter of the particles of ·003 cm., the region of transmission amounts to about 200 Å U. in the yellow, the particles being closely packed together.

Effect of the Intensity.—The region of transmission is found to widen as the intensity of the incident beam is increased and *vice versa*. If the experiment be performed with sunlight in a somewhat cloudy weather, the width of the spectrum is found to diminish remarkably as an occasional cloud passes across the sun. This observation clearly indicates that the spectral energy-curve of the transmitted light is not sharply bounded on either side of the wave-length of maximum transmission, but falls off very rapidly at first and later more slowly. The variation of transparency with wave-length could well be represented by

a graph of the same form as the well-known probability curve.

Effect of Thickness.—The region of transmission decreases as the thickness of the emulsion increases and *vice versa*, nearly the complete spectrum being transmitted through a thickness of the order of ·1 mm. The effect of varying thickness can be studied in a simple and interesting way by placing a hollow prism containing the emulsion on the table of a spectroscope, the aperture of the pencil of light passing through it being restricted by interposing a slit cut in an opaque card. As the slit is moved along the face of the prism away from its edge, the narrowing of the visible region of the spectrum is conspicuous.

Effect of Particle-size.—Emulsions in which the particles of the disperse phase are finer transmit a wider region than those containing coarser particles. The average size of the particles can be varied by adjusting the vigour and period of shaking of the emulsion either with the hand or with a mechanical emulsifier. Actually, the region of transmission was found to widen about 5 times when the average particle-size was reduced from 1 mm. to ·05 mm.

Effect of Concentration of the Disperse Phase.—The width of the transmitted spectrum alters with the concentration of the disperse phase. A very dilute emulsion transmits nearly the complete spectrum. As the concentration is increased, the spectrum becomes narrower, approaching a limit in the case of close packing.

Effect of the Relative Dispersive Powers.—All other conditions remaining the same, emulsions in which the dispersive powers of the two phases are more widely different transmit a narrower region of the spectrum. For example, this region is about half as wide in the case of an emulsion of glycerine in a mixture of carbon disulphide and acetone as in the case where glycerine is dispersed in a mixture of benzene and acetone. It need hardly be mentioned that the so-called transparent emulsions in which the two phases have nearly the same dispersive power transmit the complete spectrum.

Light-scattering by the Emulsion.—When a point source of white light is observed through the emulsion, a continuous halo exhibiting a finely-mottled structure in which the colour changes from place to place appears to surround the source which, of course, has the colour of the transmitted light, the sequence of colours in the halo depending on the region of transmission. If monochromatic light be used, the size of the halo is found to be a minimum for the wave-length

for which the two phases have the same refractive index and increases on either side of this region. Further, the size of the halo (1) increases with the intensity of the incident beam, showing that the distribution of intensity about the centre must be here also of the error-law type; (2) increases with the thickness of the emulsion; (3) decreases with an increase in the size of the particles; and (4) increases with the concentration of the disperse phase.

The spectrum of the light scattered in directions variously inclined to that of incidence may be observed by focussing it on the slit of the spectroscope. When the direction of scattering differed a little from that of incidence, the spectrum observed was quite narrow, possessing a narrow dark line in the middle corresponding to the middle of the region of transmission. At greater obliquities, both the bright and dark parts of the spectrum widened considerably.

3. *Theory of Light Propagation in Non-Homogeneous Emulsions.*

An explanation of the observed variations of transparency of the emulsions may be attempted on the principles of the wave-theory in the following way.

Let us suppose a plane wave to be incident on a cell containing the emulsion. As it passes through, any specified element of its area would encounter the particles of the disperse phase, and would thereby be retarded to an extent depending on the number of such encounters, the size of the particles, and the difference of refractive indices. On account of the random distribution of size amongst the particles, the number of encounters and therefore the retardation corresponding to the different portions of the wave-front will be different. The total area of the portions of the wave-front corresponding to the range of encounters lying between $m+x$ and $m+x+dx$ may be assumed to be proportional to $\exp.-\left(\frac{x^2}{2m}\right)dx$, m being the most probable number of encounters. If the average path through the disperse phase for a single encounter be p, the average vibration due to a unit area of the complete wave-front will be

$$y=\frac{\int_{-\infty}^{+\infty}\exp.-\left(\frac{x^2}{2m}\right)\cos\left\{wt-\frac{2\pi}{\lambda}(\mu-\mu')xp\right\}dx}{\int_{-\infty}^{+\infty}\exp.-\left(\frac{x^2}{2m}\right)dx},$$

where μ and μ' are the refractive indices of the two phases for wave-length λ.

This gives for the average intensity

$$T = \exp.-\left[4\pi^2 m\left(\frac{\mu-\mu'}{\lambda}\right)^2 p^2\right]. \quad . \quad . \quad . \quad (1)$$

If we assume a close packing, m would be approximately equal to the thickness t of the emulsion considered divided by d, the average diameter of a particle. To determine p, we have first to take the average of the paths corresponding to the various elements of the surface of a particular droplet, and then again take the average for the various sizes of the particles. This can be easily seen to be $p = \frac{2d}{3}$, where d is the average diameter of a particle.

Substituting for m and p in (1) we get

$$T = \exp.-\left[\frac{16}{9}\pi^2\left(\frac{\mu-\mu'}{\lambda}\right)^2 td\right] \quad . \quad . \quad . \quad . \quad (2)$$

To test equation (2) the following arrangement of apparatus was employed. The light from a strong source a few millimetres square in area passed through the cell containing the emulsion, the aperture of the pencil being restricted to about 1 cm., and formed an image of the source on a distant screen containing a small hole $\frac{1}{2}$ mm. diameter. The light passing through fell upon one of the windows of a Hilger-Nutting spectrophotometer, placed at a distance of about 30 cm. behind the last screen. The size of the apertures used and their distance apart are matters of great importance in order to ensure that in the light entering the spectrometer the scattered light is excluded as completely as possible. The other window of the spectrophotometer was illuminated directly by the original source, the intensity being cut down to a suitable value by an absorbing screen. The emulsion studied was one of glycerine in a mixture of acetone and benzene, and was made up of measured volumes of the liquids so chosen that glycerine comprised about 74 per cent. of the whole. Some of the results obtained are appended in the following table.

$t = 3$ cms. ; $d = \cdot 0027$ cm.

λ cms. $\times 10^{-5}$.	$\exp.-\left[\frac{16}{9}\mu^2 td\left(\frac{\mu-\mu'}{\lambda}\right)^2\right]$.	$\exp.-\left[9td\left(\frac{\mu-\mu'}{\lambda}\right)^2\right]$.	Observed Intensity.
6100	·0025	·08	·10
6080	·004	·22	·24
6040	·30	·61	·65
6020	·61	·82	·84
6000	·94	·98	·98
5980	·94	·98	·98
5960	·62	·83	·82
5940	·30	·62	·74
5920	·09	·37	·49
5900	·004	·22	·31
5880	·0025	·08	·13

In the above table, the second column contains the values as calculated from the formula derived above, and the fourth the values observed photometrically. The constant used for calculation in col. (3) is 9 instead of $\frac{16}{9}\pi^2$. On account of the vast reduction in the quantity of light due to the several small apertures, the photometric observations could not be carried out very accurately. The values in col. (3) agree much better with the observed values than those in col. (2). This discrepancy is probably due to scattered light still getting into the apparatus, which fact will certainly increase the values of observed intensities at every part of the transmitted spectrum, the difference being more marked towards the two ends, as there the real intensity due to the transmitted light itself would be very small.

Refractivity of the Emulsion.—If a wave of light be incident on the emulsion, its path will lie partly through the disperse phase and partly through the continuous medium. The emulsion as a whole will therefore have a definite refractive index and dispersive power of its own as distinct from those of either phase and of course intermediate between them. Following up the considerations set forth above, we can find expressions for the refractive index and dispersive power of the emulsion in terms of the corresponding quantities for the two phases. The total average path through the disperse phase will be the product of the average or most probable number m of encounters

and the average path p for a single encounter. This will give $\frac{2t}{3}$ for the total average path through the disperse phase, the remainder of the path $\frac{t}{3}$ lying through the continuous medium. If μ and μ' are the refractive indices of the disperse and continuous phases respectively, the refractive index μ_e of the emulsion will be

$$\mu_e = \frac{2\mu}{3} + \frac{\mu'}{3}.$$

The dispersive power of the emulsion will also be given by a similar expression,

$$d_e = \frac{2d}{3} + \frac{d'}{3}.$$

These relations were tested in the following way, using the emulsion of glycerine in a mixture of acetone and benzene. The angular dispersions between the two extreme bright green lines of the copper arc were measured with a spectrometer for the glycerine, the mixture of acetone and benzene, and the emulsion, putting them successively in the same hollow prism. The transmission through the emulsion was adjusted in the green. As the region of transmission is very narrow, two wave-lengths farther apart could not be used and the dispersions could not be greater. The results of the observations made are given below :—

Mean d.		Mead d'.		$\frac{2d}{3} + \frac{d'}{3}$.		Observed mean d_e.	
min.	sec.	min.	sec.	min.	sec.	min.	sec.
3	10	6	30	4	17	4	50

4. *Theoretical Discussion of Light-scattering by Emulsions.*

Since the droplets in the emulsions are considerably larger than the wave-length of light, the distribution of the scattered light in the halo may be determined by considerations of geometrical optics only. For simplicity, we shall consider only the deviations by refraction occurring when a ray passes through a droplet, ignoring internal and external reflexions, etc.*

* For a detailed study of the optical effects occurring when light passes through a droplet suspended in a medium of nearly equal refractive index, see N. K. Sethi, Phil. Mag. xlii. p. 669.

The deviation of a ray consequent upon successive encounters with a large number of particles of the disperse phase would be determined by the laws of probability ; the problem is mathematically the same as the well-known case of the random walk *. If α be the average deviation of a ray at a single encounter, the probability that after n encounters the angle between the original and final directions of the ray will lie between θ and $\theta+d\theta$ will be given by

$$\frac{2}{n\alpha^2} \cdot \exp.-\left[\frac{\theta^2}{n\alpha^2}\right] . \theta\, d\theta.$$

The area on a screen receiving the scattered rays between directions θ and $\theta+d\theta$ will, however, be proportional to $\theta d\theta$ for small values of θ. The intensity of the scattered light in direction θ will then be given by

$$\mathrm{I} = \text{const.} \exp.-\left(\frac{\theta^2}{n\alpha^2}\right).$$

In the case of a closely packed emulsion, $n=\frac{t}{d}$. To determine α, we have first to find the value of the deviation for a given angle of incidence i, and then take the average in the manner employed for evaluation of p in equation (1). If we remember that the deviation $d\theta$ at a single encounter is small, we have directly from Snell's law

$$de = \frac{2(\mu-\mu')}{\mu} \tan i,$$

the number 2 corresponding to the two refractions occurring at each encounter. The average value α taken over the various angles of incidence can then be seen to be $\pi\left(\frac{\mu-\mu'}{\mu}\right)$.

Substituting these values of n and α, we have

$$\mathrm{I} = \exp.-\left[\frac{d\mu^2}{\pi^2 t(\mu-\mu')^2} . \theta^2\right] \times \text{const.} \quad . \quad . \quad (3)$$

To test (3), a general value B for the numerical constant was assumed in place of $\frac{1}{\pi^2}$. B was then determined in the following way. A narrow beam of monochromatic light (the green of the mercury arc) was allowed to fall on the cell containing the emulsion, the refractive indices of the

* Rayleigh, Scientific Papers, vol. v. p. 256 & vol. i. p. 495.

two phases being made equal for the yellow lines. A screen was placed at a distance of a few cms. from the cell. The size of the halo on the screen depends upon the intensity of the beam employed. By using two small circular apertures of different diameters l_1 and l_2 in the path of the light, beams of intensities proportional to l_1^2 and l_2^2 were obtained and the angles θ_1 and θ_2 corresponding to the boundary of the halo in the two cases were measured. Assuming that the intensity at the boundary corresponds to a certain minimum perceptible value for a given wave-length,

$$l_1^2 \cdot \exp.-\left[\frac{Bd\mu^2}{t(\mu-\mu')^2}\theta_1^2\right] = l_2^2 \cdot \exp.-\left[\frac{Bd\mu^2}{t(\mu-\mu')^2}\theta_2^2\right],$$

from which B can be easily calculated.

The values of B as measured were ·08 and ·13, which are in fair agreement with the theoretical value $\frac{1}{\pi^2}$.

5. *Homogeneous Emulsions.*

The homogenization was effected by the process of sedimentation. It is well known, according to Stokes' law, that the constant velocity with which a particle falls in a liquid is greater the bigger the particle. If, then, we have a long column of rather thin freshly shaken non-homogeneous emulsion, a natural and at least partial homogenization of the emulsion will occur as the result of sedimentation, the particles being arranged in different layers more or less according to their size, the coarser particles mostly going into the lower layers and the finer remaining in the upper ones. The homogenization will, of course, be complete only in the topmost layers. Pl. V. figs. 1 and 2 are microphotographs of the sedimented emulsion taken at two different depths. The total length of the column was about 15 cm., and the length occupied by the emulsion after complete sedimentation 5 cm. The two figures correspond respectively to distances about ·3 and 2 cm. below the top. As the contrast obtained in the ordinary chromatic emulsion is too delicate to be successfully photographed, an opaque emulsion of glycerine in acetone was employed for the purpose. A drop or two of the emulsion was sucked off with a fine syringe from the desired depth. Fig. 3 is a photograph of the non-homogeneous emulsion.

So far as the transmitted light is concerned, these emulsions exhibit properties somewhat similar to those of the non-homogeneous type. The diffraction halo, however,

exhibits some very remarkable features for some distance below the surface of separation, which we will now proceed to describe. The ordinary continuous halo of the non-homogeneous emulsion gives place in this case to a beautiful system of maxima and minima, the rings increasing remarkably in size as the surface of separation is approached. The region surrounding the source is dark, then follows a fairly sharp bright ring bluish on the inside and reddish on the outside. This first ring is quite easy to observe, but, with a little practice, a second and sometimes a third bright ring also can be clearly seen even with the hand-shaken emulsion. If, however, the shaking be done by means of a mechanical emulsifier, the rings are more distinct and larger and the second ring can be seen very easily. It is, however, interesting to note that even in white light all the colours are not equally prominent in the ring system. As a matter of fact, at first sight the rings appear to have only the colour of the directly transmitted light, the other colours on either side being too faint to be easily distinguishable. If, however, a monochromator is employed for the observations, the ring system can be observed over a large part of the spectrum and the influence of wave-length on the size of the rings as well as on the intensities of their maxima can be conveniently studied. For the wave-length for which $\mu = \mu'$, the scattered light is found to vanish altogether. On either side of this point the rings reappear, the intensity of the maxima first increasing and then diminishing again. Far away from the region of direct transmission, the ring system cannot be observed at all. Moreover, the size of the rings increases continuously with increase of wave-length. Strangely, this size is not at all influenced by the thickness of the emulsion. Pl. V. fig. 4 is a photograph of the phenomenon taken with the violet light of the mercury arc. The width of the incident pencil was restricted by the use of a small aperture before the cell containing the emulsion.

To get a good picture, the region of transmission has to be carefully adjusted. The exposure given was 30 minutes. With much longer exposure, the volatile liquids composing the emulsion evaporate partly, and the adjustment is altered. It was for this reason that a denser photograph could not be obtained. Even as it is, the photograph shows the first ring clearly and the second ring is also faintly visible. The bright line across is due to some scratches on the surface of the cell.

Theory of the Diffraction Rings.—An explanation of this interesting phenomenon may be attempted in the following

way. As has been mentioned, at a given depth in the homogeneous emulsion the particles are all more or less of the same size. Consequently there is now no randomness in their distribution, and the exponential law (equation 3) no longer holds good for the distribution of intensity in the halo. On the other hand, due to their more regular spacing, the waves scattered from the various particles will be in a position to interfere, giving the observed maxima and minima, the maxima being comparatively sharp on account of the large number of particles taking part, analogous to a large number of lines in a diffraction-grating. The reason why all the colours are not equally represented in the ring system is that the light scattered by any particular row of particles in a given layer has to pass through the whole layer, partly before and partly after diffraction, and only the wave-lengths near about the point $\mu=\mu'$ have a chance of getting through. This would at first seem to mean that the intensity of the halo should be a maximum for the values of λ in the immediate neighbourhood of $\mu=\mu'$; but if we remember that the total scattered light in this region would be small also, we shall be able to understand why the brightness of the ring system first increases as we pass from the point $\mu=\mu'$ and then diminishes again.

A mathematical expression for the size of the rings can be easily obtained if we remember that in a closely packed emulsion the distance between the adjacent diffracting centres will be equal to the diameter of the particles. This would give for the angular distance θ_n from the centre, in the case of the nth maximum the relation

$$\sin\theta_n = n\lambda/d. \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

To test equation (4), θ_1 for the first ring was measured by getting its image on the ground-glass screen of a camera focussed for infinity and placed quite close to the emulsion. A narrow beam of intense light was passed through the emulsion at a suitable definite point. A set of observations taken is given below.

$$\lambda = 6\times10^{-5}\text{ cm.}; \quad d = \cdot002\text{ cm.}$$

From equation (4):

$$\theta_1 = \sin\theta_1 = \cdot03\text{ radian.}$$

$$\theta_1\text{ as observed} = \cdot025\text{ radian.}$$

The agreement is fairly close, considering the difficulties involved in the accurate measurement of d.

Surface-Colours. Another optical effect exhibited by the emulsion on settling down is the sparkling colour observed at the boundary plane between the settled emulsion below and the clear liquid above. This colour is observable from both the sides of the boundary surface at nearly grazing incidence. It changes in a beautiful way with the direction of observation, and also depends upon the colour of the light transmitted through the emulsion. A spectroscopic study of the light reflected from the two surfaces was made by the writer. For this purpose the surface was illuminated with light coming from a horizontal slit and observed through a direct-vision spectroscope with the slit horizontal. The emulsion used was that of glycerine in a mixture of acetone and benzene. The transmission was adjusted to be in the middle green. In the case of reflexion from the upper surface, the usual spectrum with the exception of a dark band in the green was obtained at moderate obliquities. At greater obliquities, however, there was a remarkable brightening of the spectrum first in the violet, which gradually extended itself towards the dark band in the green. No such brightening was, however, observed on the red side. On the other hand, reflexion from the lower surface showed a similar brightening on the red and none on the violet side. These effects may be explained in the following way. As we have seen in sect. 3, the emulsion as a whole possesses a definite dispersive power different from that of either phase. The refractive index of the settled emulsion below will therefore be different from that of the mixture of acetone and benzene above except, of course, for the transmission region in the green. It will have a lower refractive index towards the violet and higher towards the red, in this particular case, than the upper liquid. Consequently at suitable angles, which will be very near grazing, since the two dispersive powers are only slightly different, the light towards the violet side of the green will be totally reflected from the upper surface and that on the red side from the lower surface. The dark line always present in the green is due to perfect transmission and therefore complete absence of reflexion in that region, on account of the equality of refractive indices there.

6. *Summary.*

The paper describes the results of a detailed theoretical and experimental study of the optical properties of chromatic emulsions.

1. *Non-homogeneous Emulsions.*

(*a*) The range of wave-lengths transmitted by these emulsions, which is generally narrow, has been found to depend upon the intensity of the incident light, the thickness of the emulsion, the average particle-size, concentration of the disperse phase, and the difference in the dispersive powers of the two phases.

(*b*) A theoretical treatment, based on the principles of the wave-theory and the theory of probability, has been given as regards the intensity of the transmitted light. The expression obtained is

$$I = \exp.-\left[\frac{16}{9}\pi^2 td\left(\frac{\mu-\mu'}{\lambda}\right)^2\right].$$

(*c*) It has been shown both theoretically and experimentally that the emulsion as a whole has a definite refractivity of its own related to that of the two phases by a simple formula.

(*d*) An expression has been obtained for the distribution of intensity in the halo from considerations of geometrical optics and the laws of chance. This has been verified.

2. *Homogeneous Emulsions.*

(*a*) The emulsions containing particles of uniform size are obtained by the process of sedimentation. The light scattered by these emulsions does not give a continuous halo but is concentrated in well-defined circular diffraction-rings, the effect being somewhat similar to that obtained with monochromatic X-rays in the powder method of crystal analysis. The expression $\sin\theta_n = n\lambda/d$, obtained for the angular diameter of the first ring, has been verified.

(*b*) The surface of separation between the sedimented emulsion below and the clear liquid above shows sparkling colours on both the sides. A spectroscopic study shows that they are due to total reflexion, the emission as a whole possessing a different dispersive power from that of the clear liquid above.

In conclusion, the writer has much pleasure in recording his indebtedness to Prof. C. V. Raman for his invaluable guidance throughout the course of the work, which was carried out at the Laboratory of the Indian Association for the Cultivation of Science.

Calcutta,
July 23rd, 1925.

XXV. *The Pressures developed on Explosion of Gaseous Mixtures at High Densities.* *By* W. T. David, *Sc.D., M.Inst.C.E., Professor of Engineering, University of Leeds* *.

IN a recent paper by Bone, Newitt and Townend † it is shown that during the explosion of inflammable gaseous mixtures contained in a closed vessel the ratio of the maximum pressure developed to the initial pressure of the mixture before explosion increases to a marked extent as the initial pressure increases. Thus this ratio for a 28·5 per cent. mixture of hydrogen and air increases from 7·7 when the initial pressure of the mixture is 3 atmospheres to 8·82 when the initial pressure is 150 atmospheres—an increase of 14·3 per cent.; while with mixtures of carbon monoxide and oxygen diluted with argon, nitrogen, oxygen, or carbon monoxide the increase in the ratio when the initial pressure is varied through the same range is practically twice as great.

Professor Bone and his collaborators regard this increase in the ratio with initial pressure as "unexpectedly large," and they suggest that it may be due to the "increasing opacity of the gaseous medium with pressure to radiation emitted during the explosion."

If I understand their views correctly, their suggestion is that on account of increasing opacity to radiation with mixture density the gaseous mixtures during the explosion period do not lose so large a proportion of their heat to the cold walls at high densities as at low densities, and consequently in the high density mixtures a larger proportion of the heat of combustion remains at the moment of maximum pressure than in the low density mixtures. My experience of radiation measurements in gaseous explosions leads, however, to the conclusion that this hypothesis could not account for more than a small fraction of the increase in the pressure ratio because, although the rate of heat loss by radiation may be very great during the explosion period, this period is so small in the experiments that the total heat loss cannot be a very appreciable fraction of the heat of combustion of the gaseous mixtures.

There are probably several causes contributing to the

* Communicated by the Author.

† Proc. Roy. Soc. cviii. p. 393 (1925).

development of higher pressure ratios with increasing density. Among them may be mentioned the following :—

(i.) The departure of gases from Boyle's law.

(ii.) The more rapid attainment at the higher densities of equilibrium conditions between the vibratory and rotational and translational energies of the molecules constituting the products of combustion.

(iii.) A smaller relative heat loss in the denser mixtures during the explosion period.

(iv.) A smaller proportion of dissociation in the high density mixtures.

(v.) More complete combustion in the denser mixtures at the moment of maximum pressure.

(vi.) A decrease in the specific heat of the gaseous products of combustion at the high temperatures developed as the density of the gaseous mixtures increases.

I believe that causes (i.) to (iv.) are relatively unimportant and that the main causes responsible for the increase in the pressure ratio with density are (v.) and (vi.).

In regard to (v.) a study of the explosion and cooling curves taken by Bone, Newitt and Townend at varying initial pressures will, I think, offer convincing proof that combustion is more complete at the moment of maximum pressure as the density increases. An examination of the series $2CO + O_2 + 4Ar$ and $2CO + O_2 + 4O_2$ at initial pressures varying from 3 atmospheres to 75 atmospheres* will be particularly illuminating in this connexion, and indeed Professor Bone and his collaborators agree that their experiments show distinct evidence of "after-burning" (or incomplete combustion at the moment of maximum pressure) at the lower densities †.

But it is in regard to (vi.) that I wish particularly to direct attention in this paper. Some experiments of mine indicate that the specific heat of gases like CO_2 and steam which emit (infra-red) radiation when heated and which constitute the products of combustion of the exploded mixtures, decreases to a considerable extent as the density increases at temperatures at which they emit radiation strongly; and it seems to me that this is one of the main causes—possibly the main cause—of the increase of the ratio of the maximum

* Proc. Roy. Soc. A, cv. pp. 418 & 422 (1924).
† Proc. Roy. Soc. A, cviii. p. 402 (1925).

pressure developed to the initial pressure as the initial pressure increases.

As this is a point of considerable importance it is desirable to describe briefly the experimental basis for the suggestion.

I found that the intrinsic radiance from a layer of gaseous mixture after explosion of thickness inversely proportional to the density decreased at any given temperature as the density increased when the value of the intrinsic radiance was corrected for absorption*. The following table, which relates to the 15 per cent. mixtures of coal-gas and air after explosion, shows this clearly †.

Mean absolute temperature of gaseous mixture (°C. abs.).	Intrinsic radiance corrected for absorption from:—			
	2 cm. at $\frac{1}{2}$ atmosphere density.	1·33 cm. at $\frac{3}{4}$ atmosphere density.	1 cm. at 1 atmosphere density.	0·8 cm. at $1\frac{1}{4}$ atmosphere density.
2300	0·41	0·42	0·39	0·37
2200	0·38	0·4	0·36	0·32
2000	0·32	0·33	0·27	0·27
1800	0·23	0·21	0·20	0·19

Great accuracy is not claimed for the values of the corrected intrinsic radiance given in this table because (except in one case) they have been calculated from observed measurements of the intrinsic radiance from two thicknesses of the gaseous mixtures only. I think, however, they show definitely that at any given temperature the intrinsic radiance corrected for absorption from thicknesses of the gaseous mixtures inversely proportional to the density decreases to a considerable extent as the density increases—even within the limits of density $\frac{1}{2}$ atmosphere to $1\frac{1}{4}$ atmospheres.

Now since all the gaseous mixtures were of the same composition, thicknesses inversely proportional to the density contained the same number of radiating molecules (mainly CO_2 and steam) and since the intrinsic radiance values have

* The value of the intrinsic radiance corrected for absorption from a layer of gas is that which would have been actually measured had the gas been perfectly transparent.

† This table has been taken from a paper written in 1911 (Phil. Trans. A, ccxi. p. 406). Full information relating to the experimental method will be found in that paper.

been corrected for absorption, it will be clear that the figures given in the table are proportional to the radiation emitted per radiating molecule under the conditions indicated in the table. Thus the radiation emitted per radiating molecule when the gaseous mixtures are at any given temperature decreases as the density of the gaseous mixture increases, and therefore at any given temperature the vibratory energy contained by these molecules decreases as the density of the system containing them increases.

Accepting this result it will at once be clear that the specific heat of gases like CO_2 and steam will decrease as the density increases at temperatures at which they emit infra-red radiation, in other words, at temperatures at which the vibratory degrees of freedom share in the heat motion of the molecules, for the specific heat of a gas is of course dependent upon molecular vibratory energy as well as upon translational and rotational energy.

In previous papers (Phil. Mag. Feb. 1913, p. 267, and May 1920, p. 551) I have attempted to show how these results may be explained in terms of the kinetic theory of gases, and a reference to those papers will show that for any given temperature the molecular vibratory energy, and therefore the specific heat, tend towards a minimum value at very high densities. This is in accord with the experiments of Bone, Newitt and Townend, for they show that the pressure ratio tends towards a constant value at the higher densities employed in their experiments.

XXVI. *The Electrification of Two Intersecting Planes.* By W. B. Morton, *M.A., Queen's University, Belfast* *.

Summary.

THE first part of this paper is concerned with the two-dimensional problem of planes of infinite length, in the direction of their intersection, but of finite breadth. This is solved by the method of conformal representation devised by Schwarz. The differential equation which expresses the transformation is found to be integrable so that the coordinates of a point in the electric field can be simply expressed in terms of the logarithmic potential and the line of force function.

* Communicated by the Author.

The following theorems relating to the distribution of the charge are proved :—

(1) Half of the entire charge is borne on the outer side of one plane together with the inner side of the other ; or,

The excess of the charge on the outer side of a plane over that on the inner side is the same for the two planes.

(2) When the two planes have equal breadths and are inclined at angle $(\pi-\gamma)$ the charge on the convex side is to that on the concave side in the ratio of

$$\tfrac{1}{2}\pi+\sin^{-1}(\gamma/\pi) \quad \text{to} \quad \tfrac{1}{2}\pi-\sin^{-1}(\gamma/\pi).$$

In particular, when the planes are equal and at right angles the outer charge is double the inner. A drawing is given (fig. 3) of the lines of force and equipotentials for this case and the distribution of charge on two rectangular planes is discussed in detail.

The analysis is, of course, applicable to the corresponding cases of fluid motion. It leads to a solution of the problem of steady flow past the two planes, when no surfaces of discontinuity are formed. This will be discussed in a following paper.

The diagrams in the second part of the paper (figs. 8-13) illustrate the familiar case of two planes of infinite breadth. Although this is discussed in all the text-books, I do not know any in which a range of figures is given, showing the progressive alteration of the field as the inclination is changed. I publish these at the suggestion of a friend in the hope that some other teachers may find them of interest. I have negatives of the drawings which I shall be glad to lend to any who wish to make copies.

The spiral diagram to illustrate the charge distribution is perhaps new.

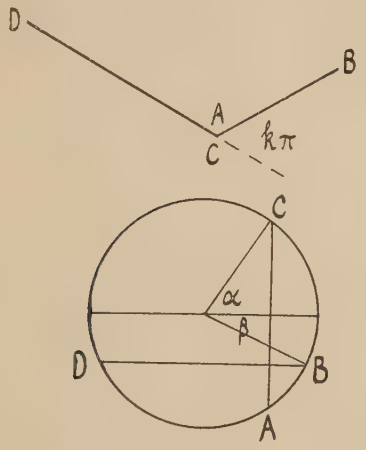
Planes of Finite Breadth.

Let the exterior angle between the planes be $k\pi$. The four faces of the two planes are to be regarded as the sides of a collapsed quadrilateral and the surrounding field in the plane of $z=(x+iy)$ is to be represented on the interior of unit circle in the plane of a second complex variable ζ (fig. 1). When this is effected the logarithm of ζ gives, in its real and imaginary parts, the potential function and the

function which represents the lines of force in the field surrounding the freely charged planes *.

If we go round the quadrilateral so as to keep the field

Fig. 1.



on the left the swerves at A, B, C, D are $k\pi$, $-\pi$, $-k\pi$, $-\pi$, respectively. Therefore the connexion between

$$z \text{ and } \zeta = \rho e^{i\varphi}$$

is given by

$$dz/d\zeta = C\zeta^{-2}(\zeta-a)^{-k}(\zeta-b)(\zeta-c)^{k}(\zeta-d), \quad . \quad (1)$$

where a, b, c, d are the values of ζ at the points on the unit circle corresponding to A B C D in the z-plane. The choice of these points is limited by the consideration that the expansion of the right-hand side for large values of ζ must not contain a term in ζ^{-1}, since obviously there cannot be a term in $\log \zeta$ in the $(z\zeta)$ relation. So we must have

$$-ka+b+kc-d = 0. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If $\phi_1, \phi_2, \phi_3, \phi_4$ are the arguments of the complex quantities a, b, c, d, the above equation gives the two relations,

$$\left.\begin{aligned} \cos\phi_2+\cos\phi_4 &= k(\cos\phi_1-\cos\phi_3), \\ \sin\phi_2+\sin\phi_4 &= k(\sin\phi_1-\sin\phi_3). \end{aligned}\right\} \quad . \quad . \quad (3)$$

* For the method, see Riemann-Weber, 'Differential-Gleichungen der mathematischen Physik,' i. p. 334. Forsythe, 'Theory of Functions,' p. 545.

On elimination of k we have

$$\tan \tfrac{1}{2}(\phi_2+\phi_4) = -\cot \tfrac{1}{2}(\phi_1+\phi_3). \quad . \quad . \quad . \quad (4)$$

Therefore the middle point of the arc $(\phi_2\phi_4)$ is separated by a quadrant from the middle point of $(\phi_1\phi_3)$. One such arrangement is shown on fig. 1, and in accordance with it we may write

$$\phi_1 = -\alpha,$$
$$\phi_2 = -\beta,$$
$$\phi_3 = \alpha,$$
$$\phi_4 = -\pi+\beta.$$

When these values are put into the two equations the cosine equation is satisfied identically and the other gives

$$\sin\beta = k\sin\alpha. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The two theorems relating to the charge on the planes follow at once from the fact that the difference between the values of the function ϕ at two points on a conductor is proportional to the total charge between the points. So the charges on the four faces are represented by the angular differences as follows :

$$\text{AB, } \phi_2-\phi_1 = \alpha-\beta,$$
$$\text{BC, } \phi_3-\phi_2 = \alpha+\beta,$$
$$\text{CD, } \phi_4-\phi_3 = \pi+\beta-\alpha,$$
$$\text{DA, } \phi_1-\phi_4 = \pi-\beta-\alpha;$$

$\therefore$ charge on CD—charge on AD

= charge on BC—charge on AB.

Again, when the breadths of the planes are equal it is obvious from symmetry that α is a right angle, and therefore

$$\beta = \sin^{-1} k.$$

So we have,

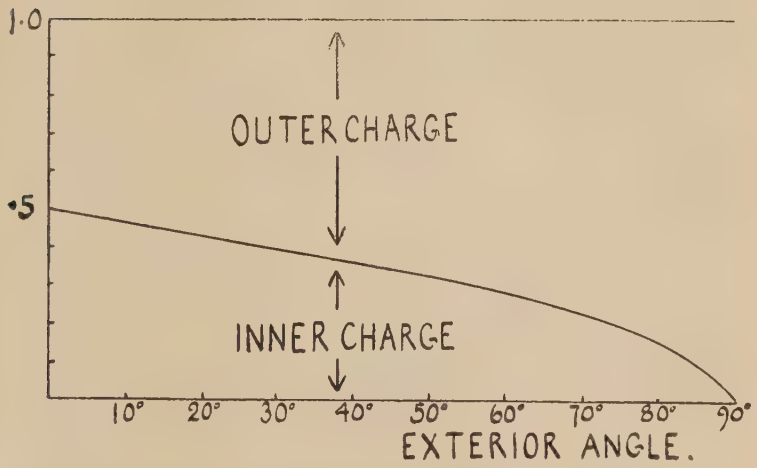
outer charge, on BC and CD : inner charge, on AB and DA

$$= \tfrac{1}{2}\pi+\sin^{-1}k : \tfrac{1}{2}\pi-\sin^{-1}k.$$

The graph (fig. 2) shows the partition of the charge between

the concave and convex sides of two equal planes at different inclinations.

Fig. 2.



To return to the differential equation, the relation connecting a, b, c, d is such as to make the right-hand side a complete differential. On identifying

$$\frac{d}{dx} \cdot (x-a)^{1-k} \cdot (x-c)^{1+k} \cdot x^{-1}$$

with

$$(x-a)^{-k} \cdot (x-b) \cdot (x-c)^{k} \cdot (x-d) \cdot x^{-2},$$

we find $$-ka+b+kc-d = 0$$

and $$ac+bd = 0.$$

The first of these is the relation already given and the second is implied in it, being equivalent to

$$\phi_1+\phi_3 = \phi_2+\phi_4 \pm \pi,$$

which is identical with equation (4).

Accordingly we find the integrated equation,

$$z = C\zeta^{-1}(\zeta-e^{i\alpha})^{1+k}(\zeta-e^{-i\alpha})^{1-k}, \quad . \quad . \quad . \quad (6)$$

Here $\zeta=\rho e^{i\phi}$, where $\log\rho+\text{const.}$ is the potential and $\phi=\text{const.}$ is the equation of a line of force. On the planes $\rho=1$, in the field $\rho<1$. The fraction k is the exterior angle between the planes divided by π, and α is determined by the ratio of the two breadths in a manner to be found later. It

is convenient to replace the constant C by $Ae^{ik\pi}$, where A is now a real constant of linear scale. This has the effect of placing the planes symmetrically so that the bisector of their interior angle has the direction of the axis of y.

For the point ϕ on the equipotential ρ the equation gives for the modulus and argument of z,

$$(x^2+y^2)^{\frac{1}{2}} = A\rho^{-1}\{1-2\rho\cos(\phi-\alpha)+\rho^2\}^{\frac{1}{2}(1+k)} \times\{1-2\rho\cos(\phi+\alpha)+\rho^2\}^{\frac{1}{2}(1-k)}, \quad . \quad (7)$$

$$\tan^{-1}y/x = k\pi-\phi+(1+k)\tan^{-1}\{(\rho\sin\phi-\sin\alpha)/(\rho\cos\phi-\cos\alpha)\} +(1-k)\tan^{-1}\{(\rho\sin\phi+\sin\alpha)/(\rho\cos\phi-\cos\alpha)\}. \quad (8)$$

The direction of the stream-line ϕ at a great distance from the planes is found by putting $\rho=0$ in the last equation. The inclination to the x-axis is then

$$k(2\alpha-\pi)-\phi.$$

To get a set of equally spaced equipotentials ρ is given a series of values in decreasing geometrical progression. Lines of force can be drawn by joining points with the same ϕ on successive equipotentials.

Fig. 3.

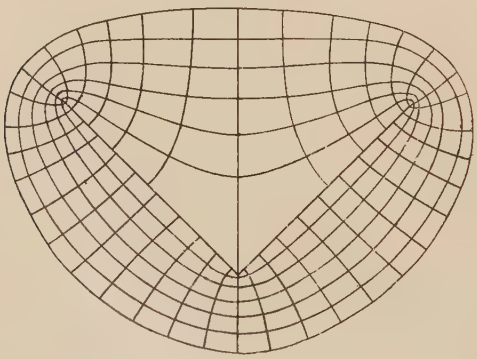


Fig. 3 shows the field for the case

$$k=\tfrac{1}{2}, \quad \alpha=\frac{\pi}{2}, \quad \rho=\cdot 9,\ (\cdot 9)^2 \ldots (\cdot 9)^6.$$

ϕ is taken at 10° intervals.

We come now to the distribution of charge on the planes and the ratio of their breadths. Here $\rho = 1$ and the surface-density, σ, is represented by $|d\phi/dz|$ which assumes the form

$$\sin^k \tfrac{1}{2}(\alpha+\phi)\, \sin^{-k} \tfrac{1}{2}(\alpha-\phi)\, (\sin\phi + \sin\beta)^{-1},$$

omitting constants. It will be seen that σ vanishes at A where $\phi = -\alpha$, and is infinite at B C D where ϕ has the values $-\beta$, α, $(-\pi+\beta)$, respectively.

For points on CD $(\phi - \alpha)$ is put for $(\alpha - \phi)$ and ϕ runs from α to $\pi+\beta$.

It remains to connect ϕ with the distance along the plane measured from the corner.

For $\rho = 1$ the expression on the right of equation (7) becomes for the right-hand plane,

$$4A \sin^{1+k} \tfrac{1}{2}(\alpha-\phi)\, \sin^{1-k} \tfrac{1}{2}(\alpha+\phi).$$

Fig. 4.

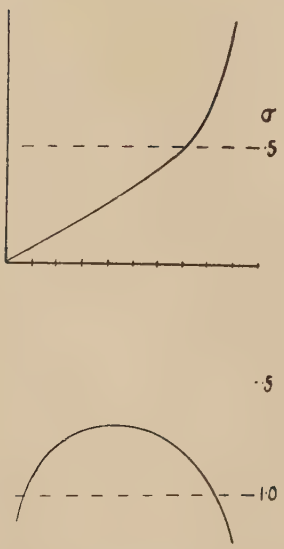
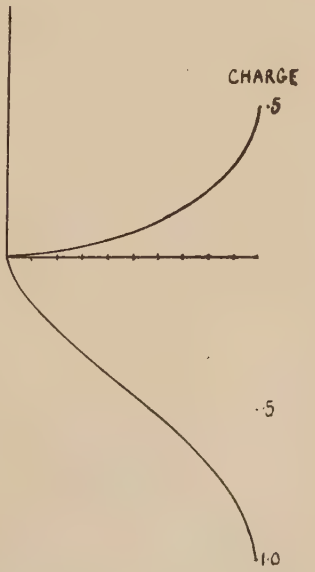


Fig. 5.



By means of these formulæ figs. 4, 5 have been plotted for the special case already dealt with. On fig. 4 is shown the surface density at each point on the two sides of either plane, and on fig. 5 the total charge between the corner and the point.

The breadth of the right-hand plane is obtained by putting $\phi = -\beta$ in the last formula, which gives

$$4A \sin^{1+k} \tfrac{1}{2}(\alpha+\beta) \sin^{1-k} \tfrac{1}{2}(\alpha-\beta).$$

For the breadth of the left-hand plane put $(\phi-\alpha)$ in the first factor and then $\phi = \pi+\beta$, with the result

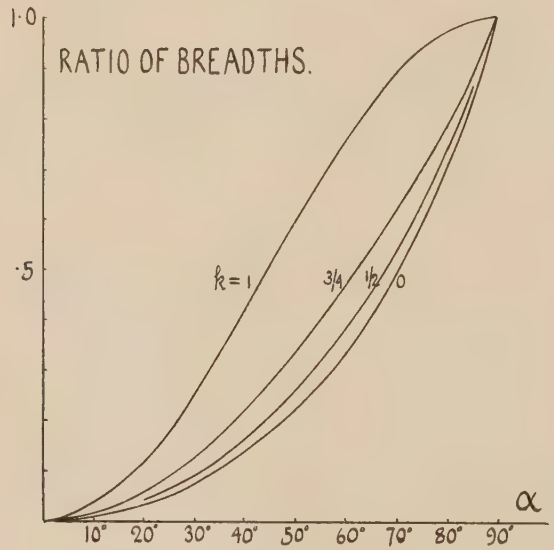
$$4A \cos^{1+k} \tfrac{1}{2}(\alpha-\beta) \cos^{1-k} \tfrac{1}{2}(\alpha+\beta).$$

$\therefore$ CB/CD

$$= r = \tan \tfrac{1}{2}(\alpha+\beta) \tan \tfrac{1}{2}(\alpha-\beta) \{\sin(\alpha+\beta)/\sin(\alpha-\beta)\}^k \quad . \quad . \quad . \quad (9)$$

with $\sin\beta = k \sin\alpha$. From this a graph can be plotted for each value of k from which can be read off the parameter α to be used for a given breadth-ratio, r (fig. 6).

Fig. 6.



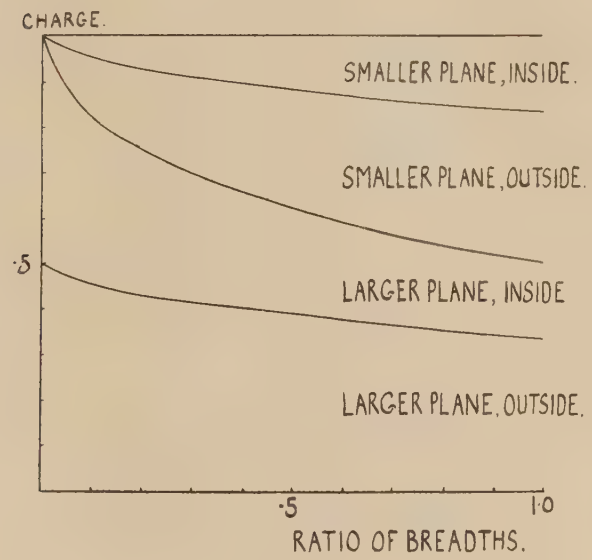
The curves fill the area between the limiting forms for $k=0$ when $r=\tan^2 \frac{1}{2}\alpha$ and for $k=1$ when $r=\sin^2\alpha$, being greatly condensed near the former limit.

When the planes make an obtuse angle, so that $k < \frac{1}{2}$, the angle α is only a little greater than $2\tan^{-1} r^{\frac{1}{2}}$.

Fig. 7 is drawn for two planes at right angles and shows how the total charge is divided into its four parts for

different ratios of the breadths. It will be noticed that the two middle segments together make up half the total charge, in accordance with the first general theorem above.

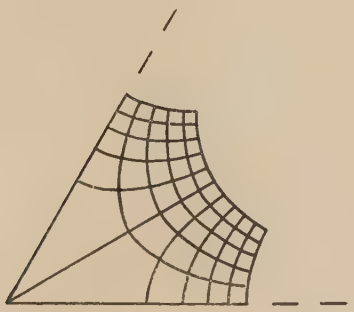
Fig. 7.



Planes of Infinite Breadth.

The series of figures 8–13 show a portion of the field at

Fig. 8.



the angle between two charged planes of infinite extent for inclinations of 60°, 120°, 180°, 240°, 300°, and 360°, bounded by an equipotential and two lines of force. The breadth of

plane taken is the same in each case, and the lines of force divide the charge upon it into five equal parts The equipotentials correspond to equal differences.

Fig. 9.

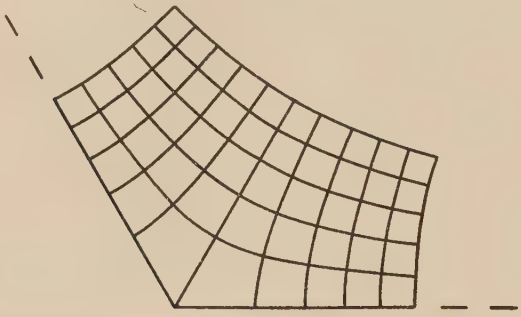
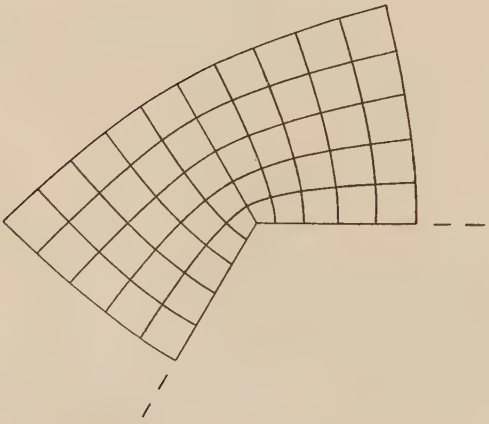


Fig. 10.

Fig. 11.



The connexion between the inclination α of the infinite planes and the distribution of charge in the neighbourhood of the hinge is usually stated in terms of the surface-density

Fig. 12.

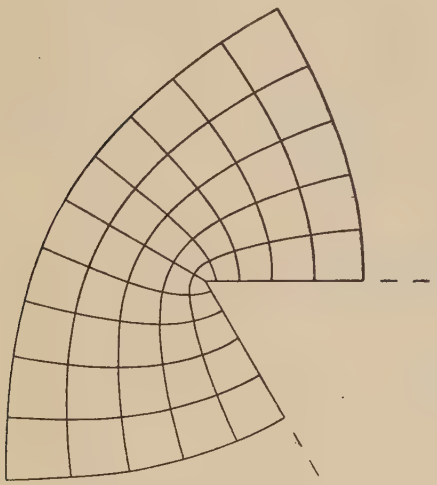
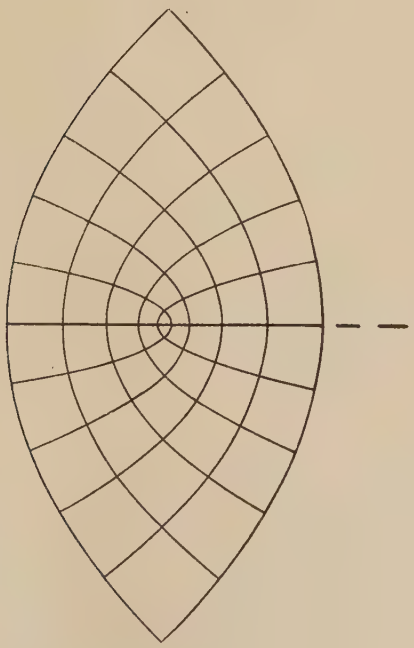


Fig. 13.



which varies as r to the power of $\left(\frac{\pi}{\alpha} - 1\right)$. This does not give a very clear physical conception of the matter, on

account of the infinite value of σ at the edge when $\alpha > \pi$. There is an advantage therefore in replacing the surface-density by the charge on a strip of plane of unit length along the direction of the hinge and given breadth. To make a definite comparison between wedges of different angles, we may suppose a fixed charge per unit length, Q_0 say, to reside on a fixed breadth, a, in every case. Then the charge on breadth r will be

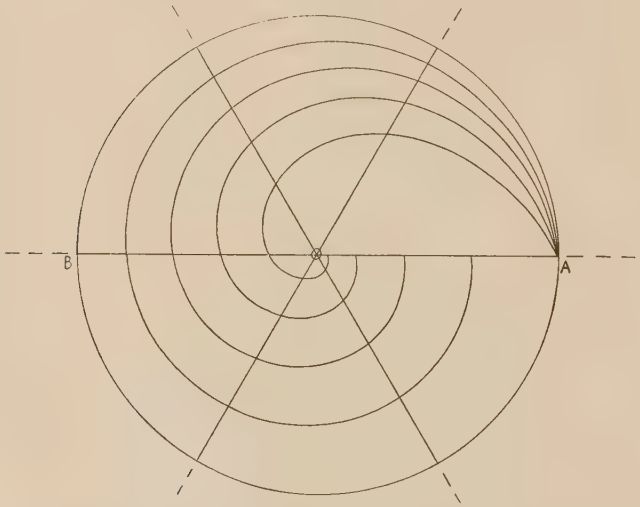
$$Q = Q_0(r/a)^{\pi/\alpha}.$$

So the breadth which carries any charge Q is

$$r = a(Q/Q_0)^{\alpha/\pi}.$$

When α is varied the locus of the end of r is an equiangular spiral.

Fig. 14.



The diagram fig. 14 illustrates this result. The distances OA, OB are each equal to 25 units. OB is divided into 5 equal parts. A circle is drawn through A and B and spirals through A and the points of division of OB. These will come round and meet OA again at distances 0, 4, 9, 16, 25. Now let OA be kept fixed while another plane, hinged at O, is rotated and let the two planes be charged. Then the circles and the spirals will divide the moving plane, in each position, into parts bearing equal charges.

XXVII. *An Improved All-Metal Mercury-Vapour Pump. By* G. W. C. Kaye, *O.B.E., M.A., D.Sc., Superintendent of the Physics Department, The National Physical Laboratory* *.

A single-stage mercury-vapour pump of the annular-jet type, made wholly of metal, has previously been described in the ' Philosophical Magazine ' †. As the result of further experiments, the pump has been considerably simplified in construction and its performance improved. These changes form the subject of this note.

Mercury-vapour pumps have displaced for general purposes almost every other type of high-vacuum pump in the Laboratory. A variety of types are now available, some of them with pumping speeds which, under favourable conditions, are extremely high. To secure this, however, it is usually necessary to have a very efficient backing pump, capable of pressures of the order of a small fraction of a millimetre. What is, however, in our experience, a greater desideratum than high pumping-speed, is for the mercury-vapour pump to be able to function to advantage when the backing-pressure is as high as a few millimetres of mercury, whether owing to a leak or to heavy-gas-emission or to an inefficient backing-pump.

One way of achieving this result is to increase the number of stages in the mercury-vapour pump. Unfortunately, this is very detrimental to simplicity of construction. A single-stage design was therefore adhered to; and the new pump is one which can be made in any good workshop. The advantages of a metal pump have already been touched on in a previous paper ‡.

Most of the details of the pump are given in fig. 1, which is almost self-explanatory. The body of the pump is made of solid-drawn steel tubing closed at the lower end. The mercury-vapour is led from the boiler by a central tube to an inverted annular jet situated in the upper water-cooled region.

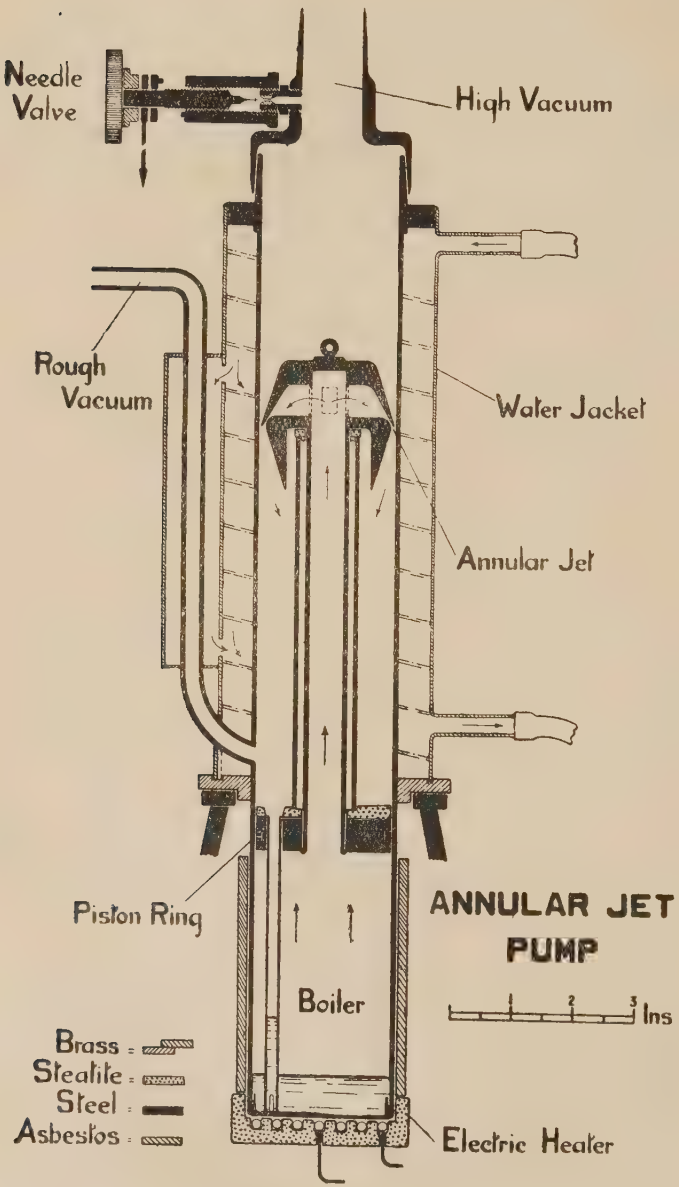
The thickness of the walls of the tubing is 1/16 inch. The bottom of the boiler, which is of the same thickness, is welded to the walls. The top of the boiler is sealed by means of a "Clupet" piston ring ; and the ring is "lapped in" much as is a ring in the cylinder of an engine, any scale being first removed. The boiler-top is thermally insulated above by a disk of baked steatite, the upper surface of which

* Communicated by the Director.

† Backhurst & Kaye, Phil. Mag. xlvii. p. 1016 (May 1924).

‡ Backhurst & Kaye, Phil. Mag. xlvii. p. 918 (May 1924).

Fig. 1.


Needle Valve
High Vacuum
Rough Vacuum
Water Jacket
Annular Jet
Piston Ring
ANNULAR JET PUMP
Boiler
1
2
3
Ins
Brass
Stealite
Steel
Asbestos
Electric Heater

is inclined so as to assist the condensed mercury to find its way back to the boiler by the return tube. Baked steatite is also used to insulate and support the tube which jackets the central vapour-tube.

Attention was paid to the shape of the two deflectors enclosing the annular jet to secure favourable expansion conditions for the jet. The widths of the jet and of the adjacent "diffusion annulus" are each 1/32 inch. A uniform diffusion annulus is secured by leaving three small outward projections equally spaced on the lip of the upper deflector. The boiler-top, the central vapour-tube, and the jet-system form a unit which can be readily withdrawn from the pump for examination.

The pump is cooled by a close-fitting water-jacket, either of brass (as shown) or steel with welded flanges. A helix of copper tape inserted in the jacket causes a swirling action of the water, the cooling being very efficacious. The water-jacket is extended some distance above the jet, so that, although the new design utilizes a greater boiler-pressure and a higher jet-velocity, there is, as compared with the old design, a marked diminution in the amount of stray mercury-vapour which finds its way to the high-vacuum side of the pump.

The improved thermal insulation of the boiler-top also permits the extension of the water-jacket almost to the level of the boiler-top, thus considerably augmenting the condensation-space below the jet, without any increase in the overall length of the pump.

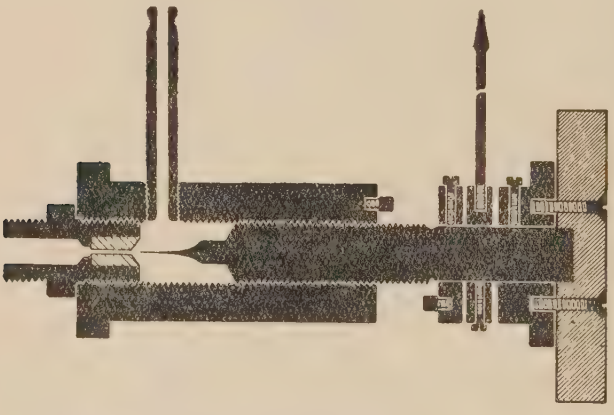
The upper end of the pump is closed with a steel cap fitted with a ground joint. A second ground joint forms the connexion between the steel cap and the glass connecting-tube of the apparatus to be exhausted. The use of sealing-wax as in the older design is thus obviated. Our experience is that such steel-to-steel and steel-to-glass joints up to $2\frac{1}{2}$ inches diameter are trustworthy and practicable for vacuum work. The merest trace of grease is necessary. We have found a taper of 4° (between sides) to have advantages and have accordingly adopted it as standard, so as to secure interchangeability of apparatus. Suitable mercury-sealing troughs are readily incorporated in the design if it is desired to avoid the use of grease in the ground joints.

Either electric or gas heating may be employed. Six hundred watts or twelve litres of coal-gas per minute can be utilized without overheating. A backing-pressure of 4 to 5 mm. is sufficient for most purposes, and the highest

vacua may be attained with a backing-pressure of $1\frac{1}{2}$ mm. The amount of mercury in the boiler is 50 c.c.; and, as a result of the reduced thermal capacity, the pump, using gas heating, will operate within three minutes from cold. It may perhaps be added that, if full advantage is to be taken of the high speed of the pump (which somewhat exceeds that of the earlier model), there should be no constriction anywhere in the high-vacuum system, and the backing-pump should be fully capable of keeping pace with the mercury-vapour pump.

A useful addition is a micrometer needle-valve for regulating the degree of the high-vacuum by means of an adjustable air-leak. The needle-valve, which is conveniently mounted in the side of the upper cap, is illustrated in fig. 2. It consists essentially of a steel needle which

Fig. 2.



MICROMETER NEEDLE VALVE.

partially or completely closes a small circular hole in a brass plug. The steel needle is conveniently turned from the solid as part of a steel spindle, from which it projects. The needle proper is about 8 mm. long and tapers slightly from a maximum diameter of a little more than $\frac{1}{2}$ mm. The hole in the brass plug is 5 mm. long and $\frac{1}{2}$ mm. in diameter throughout.

About 5 mm. of the spindle next to the needle is reduced in diameter, so that, even in the closed position of the valve, the "leakage tube" to the air is uninterrupted. The main body of the spindle is 8 mm. in diameter and is provided over about $2\frac{1}{2}$ cm. of its length with a micrometer-thread of $\frac{1}{2}$ mm. pitch. If rubber grease is employed as a lubricant, the length of screwed thread on the spindle is such as to obviate any need for a gland or seal.

The brass plug which forms the valve-seating is mounted in a steel tube, which connects the valve with the cap of the pump.

The needle readily beds itself into the brass seating, and very little pressure is needed to close the valve completely. To prevent the needle from damaging the seating by being forced beyond the closed position, an adjustable stop is provided. This may be disengaged if it is desired to open the valve more than a complete turn.

I wish to acknowledge the effective assistance given by Mr. W. H. Sewell and Mr. J. Balmanno, of the Observer staff of the Laboratory. The work was carried out partly in connexion with the programme of the Radio Research Board of the Department of Scientific and Industrial Research.

XXVIII. *An Investigation into the Theory of the "Three-Point Gap."* *By* C. E. Wynn-Williams, *M.Sc., Fellow of the University of Wales, University College of North Wales, Bangor**.

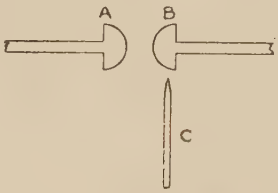
ALTHOUGH the phenomenon termed the "three-point effect" has been known for some time, and has been utilized in the construction of a form of standard spark gap, very little attention appears to have been paid to its theory. As far as the writer is aware, no theory, up to the time of writing, has been put forward which explains the effect completely.

The phenomenon is as follows. Let A B (fig. 1) be the two electrodes of a spark gap connected to an induction coil or other impulsive high potential apparatus. Corresponding to any given set of conditions, there will be a certain maximum length of gap, depending upon the peak voltage of the coil, the dimensions of the electrodes etc., for which

* Communicated by Prof. E. Taylor Jones, D.Sc.

a spark can pass regularly. If the gap is made of slightly greater length than this, the other conditions remaining the same, the spark will not pass. If, however, a third pointed electrode, C, is brought near one of the main electrodes, it is found that, under certain conditions, the spark will again pass regularly across A B, while a small spark passes from the third electrode to the neighbouring main electrode. This small spark is called the "pilot," "teaser," or "trigger" spark.

Fig. 1.



The pilot spark thus virtually lowers the impulsive sparking voltage of the main gap. Moreover, it appears to render the sparking in that gap more regular than in the ordinary two-electrode gap, so explaining the use of the "three-point gap" as a standard.

Two explanations of the phenomenon have been suggested. According to the first, ions are produced by the small pilot spark, which, travelling into the main gap, facilitate the passage of the main spark. According to the second, the pilot spark sets up oscillations in the main electrodes, which serve to cause the peak voltage periodically to rise above the critical sparking voltage, and so cause the main spark to pass.

As neither explanation appeared to have been fully investigated, it was decided to conduct experiments which, it was hoped, would establish one or other of them, or, alternatively, provide evidence on which a new theory could be founded.

The first experiments carried out were of the nature of qualitative tests to collect information as to the conditions under which the effect could be obtained.

The apparatus consisted of an ordinary two-electrode spark gap having zinc electrodes, about two centimetres in diameter and hemispherical * in shape. These were

* The main electrodes of the standard three-point gap are usually sharp points. As, however, it was found that the three point effect was much more marked when rounded electrodes were used for the main gap, together with a sharp point for the third electrode, the experiments subsequently described were carried out with this type of gap.

connected to the terminals of a small induction coil which gave a steady stream of sparks four or five millimetres in length. The length of the gap was so adjusted that the spark just failed to pass. The third point consisted of a sharp sewing-needle attached at its centre to an insulating handle of sealing-wax. It was observed that when the point of this was brought sufficiently near one of the main electrodes for a small pilot spark to pass, the three-point effect was obtained (*i. e.*, the main spark passed regularly). Moreover, it was observed that it was possible to obtain the effect when the point (and pilot spark) were moved to the extreme end of one of the main electrodes—about four inches from the main gap. It was also found possible to obtain the effect when the point was near the gap, but not sufficiently near either of the main electrodes for a pilot spark to pass, and, under certain conditions, when the point was allowed to touch one of the main electrodes. It did not seem to make any appreciable difference to which of the main electrodes the point was approached, unless one of them was earthed, in which case the point had to be brought near the other electrode.

These preliminary tests tended to the view that the phenomenon was dependent, not so much on the pilot spark (for it could be obtained without a pilot spark) as on some property of the third electrode.

Experiments made with a blunt third electrode showed that the effect was not obtained so easily as in the previous case. This appeared to indicate that a silent discharge from the third electrode might be responsible for the phenomenon in the case where it was obtained without a pilot spark.

Further experiments with an electrode sharpened at both ends tended to support this view, for it was observed that when any sharp point from which a silent discharge took place was within about five or six centimetres of the main gap, and "visible" * from it, the main spark passed regularly. This is illustrated in fig. 2, where A and B represent the main electrodes, E the main gap, and C D the third electrode, pointed at both ends.

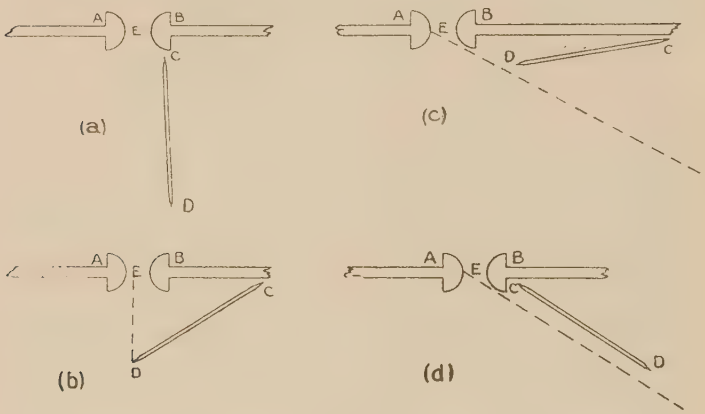
In case (*a*), the main spark was found to pass when C was brought sufficiently near to B for either (1) a pilot spark, or (2) a silent discharge, to pass from B to C, and be visible from E. If, however, C touched B, the effect ceased. In this case, D was too far from E for the silent discharge from it to affect the main gap.

* By "visible" is meant that a straight line, clear of all objects, could be drawn through the air from the point to the gap.

In case (*b*), the effect could be obtained when D was within five or six centimetres of the main gap, and (1) C touched B, (2) C was sufficiently near B for a pilot spark to pass, or (3) C was sufficiently near B for a silent discharge to pass. Here, it was the *secondary* silent discharge, at D, that was visible from E.

In cases (*c*) and (*d*), the main spark could not be made to pass under any circumstance, both discharges (at C and D) being invisible from the gap.

Fig. 2.



It was observed that if the end C of the conductor in case (*a*), and the end D in case (*b*), was covered with wax, the main spark would not pass.

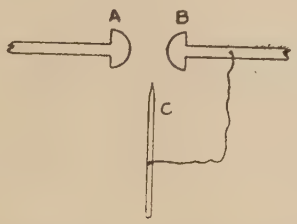
The conclusion to be drawn from these experiments appears to be that some form of discharge (silent or spark) must take place within a certain distance (about six centimetres in this case) of the main gap, and be visible from it, before the three-point effect can be obtained *.

To investigate the action of the discharge in greater detail, the apparatus was modified slightly. As the effect could be obtained (case (*b*)) with one end of the third electrode *in contact with* the main electrode, in the experiments that followed, a sharp needle, connected to one of the

* This view is supported by an observation made by Dr. J. D. Morgan ('Principles of Spark Ignition in Internal Combustion Engines,' p. 61). He finds that when the insulation of the gap is damp, the surface discharge to the earthed support is effective in lowering the impulse ratio of a two-electrode gap, but only when the discharge is on the gap side of the support (*i.e.*, presumably when the discharge is "visible" from the gap).

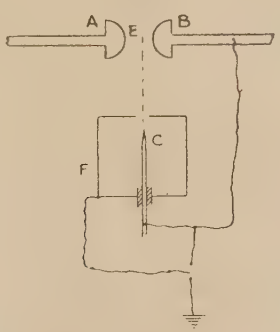
main electrodes, was used instead of the previous third electrode. This arrangement (fig. 3) produced the effect when the point was within five or six centimetres of the gap, and was found to be much more convenient in use than the previous third electrode. The experiments were afterwards repeated with another type of third electrode, which gave a pilot spark instead of a silent discharge (see p. 367).

Fig. 3.



The apparatus was set up in a dark room, and the point C carefully observed while it was brought near the gap. It was found that the main spark commenced to pass while there was yet no visible glow around the point C. When, however, C was brought nearer to the gap, a violet glow appeared. A small piece of wax placed on the end of the point was found to stop both the glow and the three-point effect, thus strengthening the view that the silent discharge from the point was necessary. This experiment was varied

Fig. 4.



by surrounding the point with a small metal chamber F (fig. 4), closed except for a small aperture so arranged that the point was visible from the gap. The chamber could be connected to earth, or to the same electrode as the point. The length of the gap was adjusted as usual to just above

the critical spark length, the chamber being connected to earth. With the point connected to the main electrode, the main spark passed regularly, showing that the phenomenon was obtained. The experiment was then repeated with the chamber connected to the same electrode as the point. It was found that the spark now failed to pass. In the first case, a silent discharge passed from the point to the earthed chamber, whereas, in the second, the point and the chamber being at the same potential, no such discharge was possible.

The fact that the three-point effect could be produced by a silent discharge as well as by a spark showed that the phenomenon was not caused by oscillations set up in the main electrodes by the pilot discharge, for such oscillations could only have been produced by the pilot discharge when the latter was a spark. The silent discharge would behave as a high resistance leak, and would give rise to no such oscillations.

The effect of interposing thin sheets of various substances between the point and the gap was next investigated. It was observed that a thin sheet of any of the substances tried (with one exception) had the effect of screening the gap from the action of the point, and so causing regular sparking at the main gap to cease. The only substance tried which was found not to cut off the effect but to be "transparent" to it, was a celluloid film, so thin as to give interference fringes when viewed by monochromatic light. Such a film was formed by allowing a few drops of a dilute solution of celluloid in amyl acetate to fall on a clean water surface and to evaporate. When such a film was picked up by means of a wire ring and allowed to dry, it was found not to cut off the three-point effect when interposed between the point and the gap *.

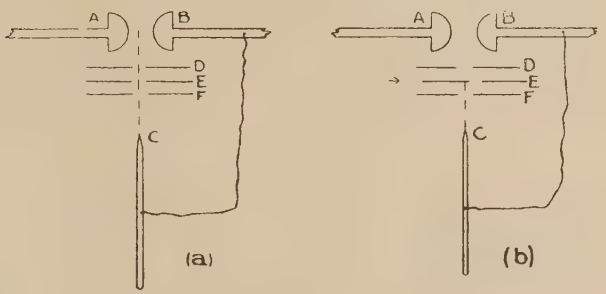
Amongst the substances tried which were found to be "opaque" were glass, quartz, mica, wood, ebonite, paper, cardboard, paraffin wax, soap films, gold leaf, metal foils and plates, etc. A small hole in any of these substances, however, would allow whatever caused the effect to pass through, provided the point, the hole, and the gap were in a straight line. It was also observed that when the screen was introduced gradually, the spark in the main gap ceased passing regularly as soon as the edge of the substance intercepted the line joining the point and the gap. These two observations seemed to indicate that as long as some part of the gap was visible, and unscreened from the point,

* Another method of producing these films is described in 'Discovery,' p. 133, April 1925.

the main spark passed regularly, and the following more elaborate experiment confirmed this.

Three small mica screens D, E, F, each perforated by a small hole, were interposed between the point and the gap and so arranged that the point, the apertures, and the gap were in alignment (fig. 5 *a*). The "effect" was found to penetrate through the apertures to the gap and render the sparking there regular. The centre screen, E, was then slightly displaced, so that its aperture was no longer in alignment with the others (fig. 5 *b*). The main spark failed to pass, showing that whatever previously affected the point could not travel from the point to the gap on account of there being now no straight line path for it. By removing

Fig. 5.



screen E, the two remaining screens with their apertures served to form a "beam" of what travelled from the point, and by displacing the system slightly, the beam was made to just miss the gap. In this case also, the main spark ceased to pass regularly.

It was evident, then, that something produced by the silent discharge travelled in straight lines from the point to the gap and so affected conditions there as to facilitate the passage of the main spark. The following explanations as to the manner in which this might have been accomplished suggested themselves :—

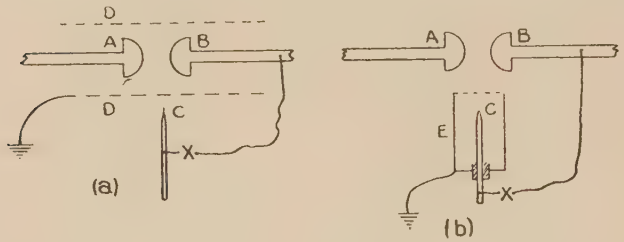
(1) The charged point, or the silent discharge, might have affected the electric field in the vicinity of the gap.

(2) Ions produced by the discharge might have travelled to the gap and so facilitated sparking there—a modification of the original explanation which assumed the ions to be produced only by the *pilot spark*.

(3) Some form of radiation might have been emitted by the discharge, which, travelling to the gap, ionized the gas there, or produced photo-electric effects at the electrodes.

With regard to (1), it is significant that very thin films of *both conductors and non-conductors* (with the one exception) cut off the effect when interposed between the point and the gap, and further, that a small hole in any of them would allow the effect to pass when the point, the hole, and the gap were in alignment. It is extremely improbable that such complete cutting off would have been obtained in all cases had the effect been due to any disturbance of the field. The following experiments, however, show that the three-point effect is obtained when the field is *not* disturbed.

Fig. 6.



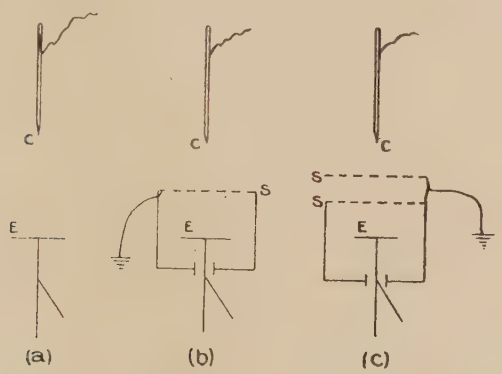
A cage of fine wire gauze, D (fig. 6 *a*), was constructed so as to surround the gap, A B, and was connected to earth. The third electrode, C, which could be connected to, or disconnected from, B, at the point marked X, was brought near the cage, and within a few centimetres of the gap. With the connexion at X broken, the coil was started and the gap length adjusted to just above the critical spark length. The connexion was then made at X, and it was observed that the main spark passed regularly. In this case, the field near the gap, being within the earthed cage, could not have been disturbed by external conditions.

The point C was then placed within, and insulated from, an earthed metal chamber E (fig. 6 *b*), having a gauze window facing the gap. The point (and chamber) was brought to within a few centimetres of the gap, and the latter adjusted as before. When connexion was made at X steady sparking resulted at the main gap. In this case, the point being within an earthed metal chamber, the only change in the electric field occurring on making connexion was within the chamber itself.

As the three-point effect was obtained in both cases despite the fact that the field near the gap was not disturbed, it is evident that disturbances occurring in the field near the gap are not necessary for the production of the phenomenon.

As regards (2), the fact that almost all substances cut off the effect completely when interposed between the point and the gap, and that ions of the same polarity as the point were liberated from the latter during the silent discharge (as could be shown by the diverging of the leaves of an electroscope brought under the point) were consistent with this view. On the other hand, as it seemed natural to conclude that the ions travelled along the lines of force radiating from the point to the electrodes of the main gap, and as the point was connected to one of the electrodes, so that these lines of force were not evenly distributed, it seems difficult to reconcile this view with the "straight line propagation" effect observed. Again, a sheet of earthed metal gauze interposed between the point and the gap, as shown in the previous experiments, allowed the point to affect the main gap. Such a screen, however, would considerably alter the distribution of the field between the point and the gap, and (if the A electrode of the gap were earthed) even reverse the direction of it, which, of course, would tend to drive ions away from the gap.

Fig. 7.



To investigate this matter further, and to ascertain whether and under what conditions ions could penetrate a gauze screen, the following tests were carried out.

The third point C was placed about six centimetres (this being the "range" of the point for the three-point effect) above the cap of an electroscope E (fig. 7 *a*). On starting the coil, the leaves of the electroscope diverged, thus showing that ions travelled from C to E and charged the electroscope. This was found to be the case whether C was connected to electrode A or B of the main gap. An earthed sheet of

metal gauze S was then interposed between C and E, and the experiment repeated. It was observed that a very slight deflexion was obtained. Suspecting that this was caused by ions travelling from C to E along lines of force round the edge of the gauze, an earthed metal collar was placed round the cap of the electroscope, and the experiment repeated with the gauze placed on this (fig. 7 *b*). It was now observed that the electroscope remained uncharged, showing that ions did not traverse the region of no field existing between S and E.

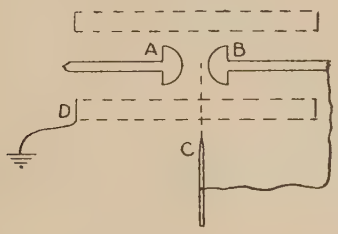
On trying this with E initially charged (so that a field existed between E and S, which was at zero potential), it was observed that : (1) If the charge on E was of the same sign as that on C, nothing happened (*i. e.*—the field between E and S, being opposed to that between C and S, ions were prevented from reaching E and altering its charge) ; and (2) If the charge on E was of the opposite sign to that on C, the leaves of the electroscope fell, and did not rise again. In case (2), the field between E and S being now in the same direction as that between C and S, the ions from C, on reaching S, were driven to E under the action of the field between S and E. Having reached E, the charges on the ions, being of opposite sign to the initial charge on E, neutralized part of the latter (as indicated by the fall of the leaves), so gradually reducing the field between S and E to zero. Then, as before, no further ions passed through S to E, as was shown by the leaves remaining undeflected.

Evidently, then, an earthed gauze screen prevented the passage of ions from C to E, provided there was either (1) no field, or (2) an opposing field, on the side furthest from the point. A double screen, constructed from two sheets of earthed gauze separated by an interval (in which no field could exist as both sheets would be at the same potential), should therefore prevent the passage of ions in all cases. This was shown to be the case, for, by placing such a screen between the point and the electroscope (fig. 7 *c*), it was observed that whatever was the original condition of E (uncharged, or charged positively or negatively) ions from C now failed to reach E and alter its charge.

A "double cage" of earthed gauze D was constructed so as to surround the gap (fig. 8), the distance between the two cylinders being about one centimetre. With this arrangement, it was observed that the point C, placed just outside the cage, could produce the three-point effect just as readily as when the cage was absent, thus showing that the passage of ions into the gap is not essential for the production of the phenomenon.

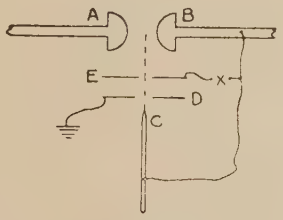
Making use of the second condition under which ions could be prevented from reaching the gap (*i. e.*, an opposing field), the following experiment was carried out. Two

Fig. 8.



small metal plates D and E (fig. 9) separated by a distance of about a centimetre, and having a small hole bored in each, were arranged between the third point C and the gap so that the point, the holes, and the gap were in alignment. Plate D (nearest the third point) was earthed, while E could be connected to or disconnected from the third electrode at the point X. By this means, when E and C were connected, so that they were at the same potential, a field was set up between D and E in the opposite direction to that existing

Fig. 9.



between C and D. As was shown in the previous experiments, such a field would prevent ions from C from reaching the gap. The connexion at X being broken, the third point was found to render the passage of the main spark regular. The connexion was then made at X, and no difference was observed in the regularity of the passage of the main spark. This seems to indicate, as before, that the three-point effect is independent of the passage of ions from the point to the gap.

Two other observations tend to confirm this view. In the first place, when the gauze screen S (fig. 7 *b*) was replaced by the celluloid film already referred to (which did not cut

off the three-point effect), it was observed that the electroscope E retained its charge (+ or −), showing that such a film, while allowing the point to affect the gap, effectively stopped the passage of ions. Secondly, while the third point could only produce the phenomenon when within about six centimetres of the gap, it was observed to be capable of producing a deflexion of the leaf of an electroscope placed as far away as eighteen centimetres. If, therefore, the effect had been due to ions, the point should have been capable of producing the three-point effect at greater distances from the gap than six centimetres. Further experiments with a different type of third electrode referred to later (see page 368) tended to confirm this view.

As, therefore, neither ions travelling into the gap nor disturbances of the electric field in its vicinity seemed to be necessary for the production of the phenomenon, there remained to be investigated the possibility that it was due to some radiation emitted from the point, which either ionized the gas in the gap, or caused photo-electric effects at the electrodes.

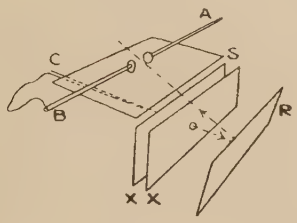
It had already been observed that whatever travelled from the point to the gap did so in straight lines, a fact which, with the screening effect obtained, was consistent with the view that it was a form of radiation. Tests were then conducted to ascertain whether it was capable of the reflexion and refraction effects usually associated with radiant energy. Great difficulty was, however, experienced at this stage of the work owing to the fact that the maximum distance that could be obtained between the third point and the gap was only six centimetres, and that all the experiments had to be carried out in this space.

As regards refraction, it was out of the question to ascertain whether the radiation obeyed Snell's law, as the only substance which was found to be transparent was, as explained, a thin celluloid film, of a thickness which gave interference fringes with monochromatic light.

To test for reflexion the experiment illustrated in fig. 10 was arranged. A and B were the main electrodes, and C the third point connected to B, and placed under the gap, pointing in a direction perpendicular to the line joining A and B. S was a screen so arranged that no "radiation" could pass directly from C to the gap, while X X were two perforated mica screens which served to direct the "radiation" into a "beam." The coil was started, and the gap adjusted to just above the critical spark length. When S was not in position, regular sparking was obtained in the

gap owing to the direct effect from the point C. The sparking ceased when S was placed in position, but recommenced when a polished glass plate R was brought near the point and so adjusted as to "reflect" the "beam" falling upon it into the gap. It was observed, however, that while reflexion results were obtained consistent with the presence of radiation, the reflexion was diffuse, and not regular. For the angle at which the mirror was held could be varied over a region on either side of the value necessary had the angle of reflexion been equal to the angle of incidence. Various substances were tried as mirrors—glass, quartz, polished metal plates, paper, cardboard, etc., and the same diffuse reflexion effects obtained from them.

Fig. 10.



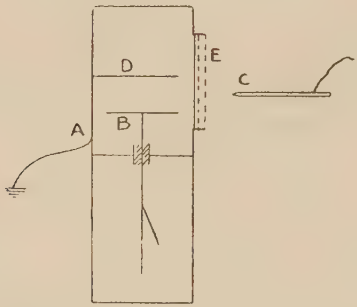
The effect seemed to be independent of the condition of the surface of the mirror,—a piece of paper held in a suitable position caused the main spark to pass just as readily as a piece of polished glass. In no case was any reflexion other than "diffuse" obtained.

As the only transparent substance was very thin celluloid, and only diffuse reflexion effects were obtainable, the radiation could not be focussed by either lenses or mirrors. Also, as the methods usually employed for determining wave-lengths utilize either reflexion or refraction effects for obtaining a double image or a spectrum, it was equally impossible to measure the wave-length of the "radiation" in the ordinary manner.

To ascertain whether the radiation ionized the air through which it passed, a simple ionization chamber was constructed as shown in fig. 11. This consisted of an earthed metal chamber A, in which was placed the electrode B of a small gold-leaf electroscope. Above and near to this was a parallel plate D, attached to the chamber. A window E, covered with a thin celluloid film and a double earthed gauze (as used in a previous experiment), while allowing

the radiation from the third point C to enter the chamber, prevented the entry of any free ions. The electroscope was charged, and the rate of fall of the leaf due to leakage was observed. The electroscope was then recharged, and the coil started so as to maintain a silent discharge from C. It was observed that, in the several experiments performed, the rate of fall of the leaf was from four to sixteen times greater (depending upon the conditions of the experiment) when the radiation was allowed to enter the chamber than when a screen was interposed between C and E, thus showing that the radiation ionized the air in the space between B and D and so increased the rate of leakage of the charge. As the

Fig. 11.



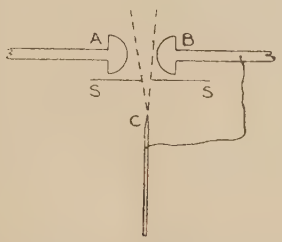
rates of fall of the leaf for positive and negative charges on the electroscope were observed to be approximately the same, it was concluded that if the radiation produced any photo-electric effects, they were small compared with its ionizing properties, for had there been any marked photo-electric effect, the rate of fall of the leaf should have been expected to be different for a negative charge on the electroscope and for a positive charge.

This is supported by the fact that the pressure in the chamber of a small amount of turpentine vapour (which is strongly ionized by "Entladungstrahlen"), increases the ionization.

The radiation being thus proved capable of ionizing the air through which it passed, the following experiment was arranged (fig. 12). The third point and the gap being set as usual, the three-point effect was obtained. In accordance with the straight line propagation effect observed, two screens SS were then placed between the point C and the gap, so as to shield the electrodes from the point, and leave exposed only a small section of the gap (*i. e.*, the gas) to

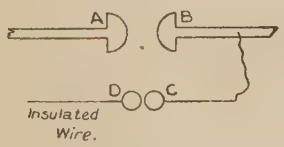
the radiation from C. It was observed that this did not affect the regularity of the passage of the main spark. As by this means ionization effects only could be obtained in the gap, it was concluded that photo-electric effects were not necessary for the production of the three-point effect, and that it was due to the ionization of the gas in the gap by the radiation emitted from the point.

Fig. 12.



So far, only one type of discharge had been investigated (viz., the silent discharge). As in certain cases the three-point effect was caused by a pilot spark visible from the gap, it remained to investigate whether the conclusions drawn for the silent discharge applied also to the spark. For this purpose, the third electrode was altered as shown in fig. 13.

Fig. 13.



A and B, as usual, were the main electrodes, set apart at just above the critical spark length, while C and D were two small spheres, about three millimetres in diameter, and separated by about half a millimetre. C was connected to the main electrode B, and D to a short length of wire. The capacity of the latter was sufficient to enable a small spark ("pilot spark"), visible from the main gap, to pass across C D when the potential rose across A B. By increasing the length of the free wire, the intensity of the pilot spark could be increased. With this arrangement, the experiments carried out with the pointed type of third electrode were repeated (with the exception, of course, of those peculiar to the silent discharge), and it was observed that *the general*

conclusions drawn for the silent discharge applied also to the spark discharge. Moreover, the radiation from this pilot spark was found to be more intense than that emitted from the silent discharge, for while the maximum distance that the point could be placed from the gap and cause the effect was only six centimetres, the pilot spark could produce the three-point effect when ten centimetres from the gap.

On bringing an uncharged electroscope near to the pilot spark gap, to investigate whether ions were liberated as in the case of the silent discharge, it was observed that the leaves were not deflected even when the cap of the electroscope was within one or two millimetres of the gap—*i. e.*, just too far away for a spark to pass to the electroscope. (In the case of the silent discharge, it will be remembered that the leaves of the electroscope were deflected when the cap of the latter was as far away from the point as eighteen centimetres.) The conclusion was therefore drawn that either (1) no ions, or (2) an equal number of + and — ions were propagated from the pilot spark to the electroscope. As, however, owing to the way in which the pilot gap was connected (*i. e.*, one electrode of the pilot gap to one terminal of the coil, the other being free) there would be an effective field between the gap and the electroscope (initially at zero potential) which would tend to deflect + and — ions in different directions, the second conclusion is extremely unlikely. This experiment therefore confirms the view that the phenomenon is not dependent upon the passage of ions into the gap (see page 364).

An interesting observation was made when the screening tests carried out in the case of the pointed third electrode were repeated with the pilot gap in place of the point. It was found that a thin plate of quartz, when interposed between the pilot spark and the main gap, while considerably reducing the regularity of the passage of the main spark, did not cut off the three-point effect completely. When, however, the electrodes of the main gap were shielded from the action of the radiation from the pilot spark, as described in a previous experiment, it was observed that the three-point effect was completely cut off by the quartz. The conclusion was therefore drawn that in the case of the pilot spark, which was rich in ultra-violet light, although the radiation ordinarily producing the ionization in the gap was cut off by the quartz plate, sufficient ultra-violet light was transmitted by the latter to cause appreciable photo-electric effects at the electrodes of the main gap, and thus maintain the slight three-point effect observed.

In the case of the silent discharge, it will be remembered, quartz was found to cut off the effect. As ultra-violet light is to be expected from this type of discharge also, the screening tests were again repeated, with a very intense silent discharge, and the distance between the point and the gap reduced to about three centimetres. In this case, it was found that a quartz plate would permit sufficient ultra-violet light from the silent discharge to reach the electrodes and so maintain a very slight three-point effect. As before, however, when the electrodes were shielded, the effect was completely cut off by the quartz.

These experiments show that the photo-electric action of the ultra-violet light emitted from an intense pilot discharge (spark or silent), while not being the main cause, assists in the production of the three-point effect.

In the case of the pointed third electrode, it was also found possible to obtain the three-point effect by connecting the sharp point to one terminal of a wimshurst machine instead of to one of the main electrodes. When the potential at the point was thus raised sufficiently high for a silent discharge to take place at the point, it was observed that the main spark commenced to pass regularly as usual. With the other "pilot gap" type of electrode (fig. 13) the three-point effect could only be obtained when the necessary potential for the production of a pilot spark was derived either from the coil supplying the main gap, or from another coil operated from the same break as the main coil. In these cases, the passage of the pilot spark was simultaneous with the rise of potential across the main gap.

Having thus traced the main cause of the three point phenomenon to the ionization produced in the gas in the main gap by the radiation emitted from the pilot discharge, it remained to identify (if possible) the radiation. As it was out of the question, for reasons already stated, to measure its wave-length in the ordinary manner, its position in the general wave spectrum had to be inferred from its observed properties. These were :—

(1) The radiation, while capable of diffuse reflexion effects, could not be regularly reflected.
(2) It ionized the air through which it passed.
(3) It was transmitted by a thin celluloid film, but not by any other substance tried.
(4) It could penetrate air at ordinary pressure to a distance of some centimetres.

Fig. 14 is a diagram representing the general wave-spectrum, in which the wave-lengths are plotted logarithmically in the vertical direction, and the approximate regions of the various known types of radiations indicated by horizontal lines. Two sections in the diagram—B, from a wave-length of 1·8 millimetres to about 0·4 millimetre, and G, from a wave-length of about 1000 Å. to approximately 13 Å, call for special attention. The type of radiation corresponding to B has been produced experimentally, although its properties have not yet been completely investigated. From the fact, however, that the properties of radiations A and C, on either side of it, are very similar, it is reasonable to conclude that the properties of radiations B do not differ greatly from them. With regard to G, an extensive section, the only known types of radiation existing in it are the "entladungstrahlen" discovered by Wiedemann *. Owing to the difficulties encountered in the experimental work, the properties of these radiations have not yet been fully investigated, but the following have been established :—

(1) They are not capable of being reflected regularly.
(2) Gases through which they pass are ionized by them.
(3) A thin celluloid film is transparent to them while most other substances are not.
(4) They penetrate air at ordinary pressure to a distance of some centimetres.
(5) They are emitted by spark, and the luminous parts of low pressure, discharges.
(6) The rays can produce "thermoluminescence" in certain "solid solutions."

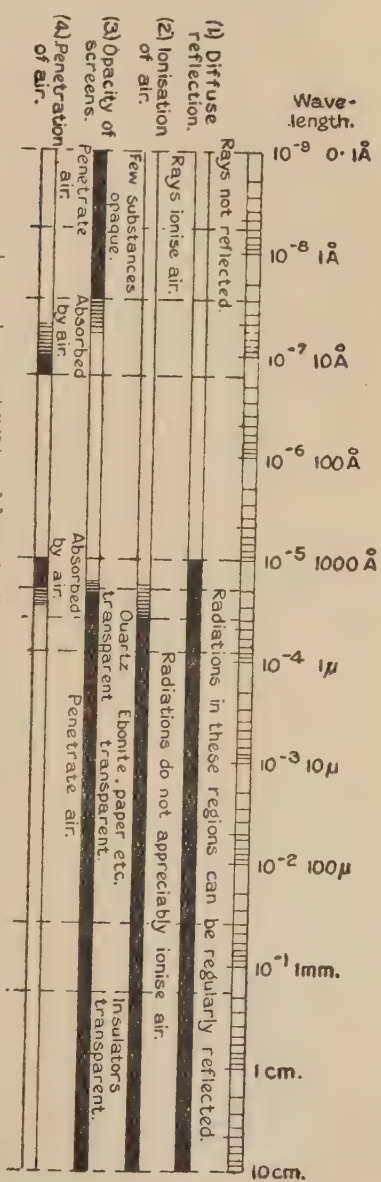
The properties of the radiations in the remaining sections are sufficiently well known, and need not be set down here.

Making use of the four properties specified for the radiation now considered, in the light of what is known of the general wave spectrum, the following conclusions may be drawn.

From (1) (no regular reflexion obtained), it is evident that the wave-length must be small, for regular reflexion effects are obtainable with polished metal, glass, quartz, etc. for radiations in sections A to F. While diffuse reflexion effects are obtained with entladungstrahlen, no

* Millikan, using a vacuum spectrograph with a ruled grating, and a high potential vacuum spark, has observed spectral lines between 1000 Å. and 136 Å. X-rays of very long wave-length lying in this region (G) have been produced by means of low velocity cathode rays and photo-electrons.

Fig. 14.



L. γ-RAYS.—Most penetrative type of radiation.

K. HARD X-RAYS.—Penetrate air and most substances; not reflected; ionize gases.

H. SOFT X-RAYS.—Low penetrative power; not reflected; longer wave-lengths absorbed by air.

G. *Region not yet fully investigated.* Entladungstrahlen (λ unknown) lie somewhere in this region: properties not fully determined; ionize gases; diffusely reflected; penetrate air; few substances transparent.

Spectral lines between 1000 Å. and 136 Å., have been observed and measured by Millikan, and very long λ X-rays have been produced.

F. SCHUMANN.—Absorbed by air and most substances; ionize gases; reflected.

E. ULTRA-VIOLET.—Ionize gases slightly; reflected; few substances transparent.

D. VISIBLE.—Non-ionizing, reflected; many substances transparent.

C. INFRA-RED.—Non-ionizing; can be reflected; substances such as quartz, ebonite, paper, etc., transparent.

B. *Region not yet fully investigated.* Properties inferred similar to those of A and C.

A. ELECTRIC WAVES.—Non-ionizing; most insulators transparent; metals opaque; reflected.

Longest wave at present in use about 30,000 metres.

The thick portions of the lines indicate the regions from which the radiation is debarred in virtue of the property under consideration. The only region, therefore, in which the radiation can lie is section G, in which no thick line appears.

reflexion is obtained with X or γ rays. (The reflexion of X-rays from crystals is of course an interference effect, and not pure reflexion.) From this it is to be inferred that the radiation cannot lie in sections A, B, C, D, E, or F. This is indicated in fig. 14 by the thick line running from A to F, opposite (1), marked "diffuse reflexion."

From (2) ("ionization of air") also, it would appear that the wave-length is small, for none of the radiations in sections A, B, C, or D are known to ionize gases. Ultra-violet and Schumann's rays exhibit ionization effects, while entladungstrahlen, X-rays, and γ-rays are strong ionizing agents. Hence, proceeding as in the case of (1), the thin and thick parts of line (2) ("ionization of air") indicate the regions in which the radiation could or could not lie as determined by this property of ionization.

Property (3) (most substances opaque, but thin celluloid transparent) furnishes evidence of a more definite character than either of the other two. Had the radiation been of the type met with in A or B, almost any insulator would have been transparent, while metals would have been opaque. The fact that such insulators as paraffin wax, glass, ebonite, paper, etc. were opaque therefore rules out this section. Similarly, as materials such as paper, ebonite, etc. (which permit the passage of infra-red rays) cut off the radiation, it is evident that the radiation is not in the infra-red region. Had it been in section D (visible spectrum), glass etc, would have transmitted it, while the fact that quartz cuts off the effect shows that it cannot be in the ultra-violet down to a wave-length of about 2000 Å. (limit of quartz = 1850 Å.). Most substances are opaque to Schumann's rays and to entladungstrahlen, so that no definite statement can be made with regard to regions F and G. The fact, however, that a thin celluloid film is transparent to the radiation is consistent with the view that it is some type of entladungstrahlen. X-rays (sections H and K) next claim attention. With the exception of soft X-rays (long wave-length) the radiations in this region have large penetrative powers. As the radiation in question was stopped by most substances, it is evident that it could not have been any form of X-ray other than one of extremely long wave-length. This fact was further verified, for on exposing to the radiation an X-ray photographic plate wrapped in paper, and developing, it was observed that no radiation had penetrated the paper and affected the plate. The time of exposure was sufficiently long for the presence of any X-ray which could ionize the

gas in the gap to be recorded on the plate. Hence it was inferred that no such radiation (*i. e.*, one capable of penetrating the paper—say of greater wave-length than a few Ångström units) was present in such intensity as to be the cause of the ionization.

Of still shorter wave-length than the X-rays are the γ-rays of radioactive substances, which are the most penetrating rays known—a fact which precludes the possibility of the radiation from the discharge being in this region. Beyond this, no further type of radiation is known. It is probable, however, that if a radiation of shorter wave-length than the γ-rays is discovered, it will be of high penetrative power. In accordance with the method applied to (1) and (2), line (3) therefore indicates that the radiation cannnot lie in sections A, B, C, D, E, nor in sections K and L.

Property (4) (penetration of air) indicates that the radiation cannot lie in sections F and H. Section F (Schumann's rays) comprises the extreme ultra-violet region, a type of radiation with general properties similar to those of ultra-violet radiations, but highly absorbed by air, especially near the low wave-length end of the region. (At a wave-length of 1000 Å. a millimetre of air at ordinary pressure will absorb the radiation almost completely.) The very long wave-length X-rays are also absorbed by air. [In carrying out investigations in these regions, vacuum spectrographs have to be used.] The thickened portions of line (4) therefore indicate that the radiation cannot lie in sections F and H.

The only range of the general wave spectrum from which the radiation under consideration is not debarred by one or more of its properties is section G (in which no thick line appears in the diagram), extending from a wave-length of approximately 1000 Å.* to about 13 Å.—a considerable range. As has already been explained, the only radiation known and examined within this region is entladungstrahlen, and its properties and wave-length have not yet been fully determined. As the wave-lengths of entladungstrahlen have not been determined, it is impossible

* As, in his experiments on spectral lines, Millikan used an artificial diffraction grating for measuring wave-lengths, it is reasonable to conclude that regular reflexion effects can be obtained with the wave-lengths he dealt with. Also, since a vacuum spectrograph had to be used, waves in this region must have been absorbed by air. These two facts appear to narrow the region in which the radiation concerned can lie, from 1000 Å.—13 Å. to 136 Å.—13 Å.

to state what position they occupy in the region. Further, the scanty information as to their properties rendered difficult the task of determining whether the rays emitted by the pilot discharge corresponded to some form of them, or to some other, hitherto unknown, radiation lying in this region. Another difficulty arose from the highly absorbable nature of the radiation, which rendered most of the tests applied of a negative character.

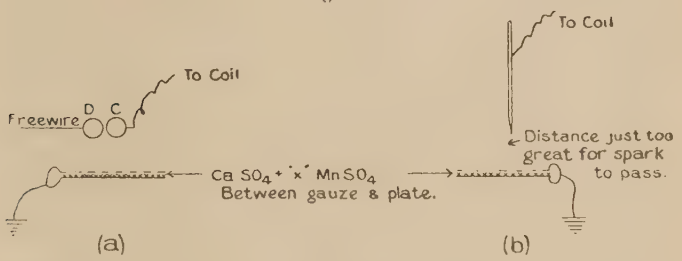
Of the six properties specified as characteristic of entladungstrahlen, it will be observed that the first four are characteristic of the radiation now considered. In addition, the fifth is characteristic when the pilot discharge is a spark. This indicated the possibility of the radiation being a form of entladungstrahlen. It remained therefore to investigate whether the sixth property of entladungstrahlen (thermoluminescence) was also a property of the radiation.

A thermoluminescent salt ($CaSO_4 +$ "x" $MnSO_4$) was prepared. Various methods of preparation were tried, but the best salt was produced when calcium sulphate was precipitated from a solution of calcium chloride by means of a solution of manganese sulphate. The precipitate was washed, dried, and heated to a high temperature for some time. As a test for sensitiveness, some of the resulting powder was placed near the main gap, so that the radiation from the main spark (which contained entladungstrahlen) fell on it. After an exposure of about half a minute, the powder was gently warmed in a dark room. A bright green glow indicated that the radiation from the main spark had excited thermoluminescence in the salt. As this phenomenon is supposed to be produced in this particular salt only by entladungstrahlen and cathode rays, it could be used as a test for the presence of entladungstrahlen when cathode rays were known to be absent.

As the "pilot gap" type of third electrode (fig. 13) (spark discharge) could affect the gap from a greater distance than could the point, it was tried first. The salt was spread in a thin layer on an earthed metal plate, an earthed gauze being placed above it (fig. 15 *a*). The pilot gap was then placed a few centimetres above this, and the salt exposed to the radiation from the pilot spark. It was observed that a definite glow could be obtained on heating after an exposure of half an hour. From this, it was clear that *while entladungstrahlen capable of producing thermoluminescent effects were emitted by the*

pilot spark, they were much less intense than those emitted by the main spark. As to this, however, it must be remembered that the pilot spark was only about half a millimetre in length, and "thin," while the main spark was about five millimetres long, and "intense." In the experiments on the properties of entladungstrahlen, the sparks used were longer than either of these *, and it had been observed that an "intense" spark gave a stronger thermoluminescence than a "thin" one of the same length. This explains why such a long exposure was needed in the case of the pilot spark.

Fig. 15.



The "pilot gap" of the last experiment was now replaced by the third point (fig. 15 *b*), which was arranged above and as near to the gauze as possible, without allowing sparks to pass from the point to the gauze (*i. e.*, so that the discharge was "silent"). The results of about twenty tests, in which the salt was exposed to the radiation from the point for various times ranging from a quarter of an hour to four hours, showed no definite evidence of the presence of thermoluminescence. In one case only, after an exposure of seventy-five minutes a very faint glow was observed on heating the salt, but as this effect was not obtained again, even with exposures as long as four hours, it was assumed that it was caused by the entladungstrahlen emitted by the stray sparks which occasionally passed from the point to the gauze.

While the thermoluminescent effects obtained in the case of the pilot spark definitely indicate the presence of entladungstrahlen in the rays emitted by the discharge, the absence of such effects in the case of the silent discharge does not necessarily imply that no entladungstrahlen are present. In the first place, it is conceivable that entladungstrahlen might be present of intensity sufficient

* E. Laird (Phys. Rev. 1910, i. p. 293) employed a spark of 1·5 cm.

to produce ionization effects, but not to affect the salt to such an extent as to produce visible thermoluminescent effects. The view is consistent with the observed fact that ionization effects are more readily obtained than thermoluminescent effects. It is also to be remembered that the radiation from the silent discharge was not so intense as that emitted from the spark, as the latter could penetrate a layer of air ten centimetres thick, while the former could penetrate only six centimetres.

Secondly, it is possible that the radiations emitted by spark and silent discharges while both within the same region G, may be of different wave-lengths. Ionization effects are to be expected from any radiation within this region, as most low wave-length radiations ionize gases. On the other hand, thermoluminescence is most probably a phenomenon produced only by particular wave-lengths, or ranges of wave-length. If such is the case, the absence of any thermoluminescence in the case of the silent discharge could be explained by assuming that while there is present a radiation capable of ionizing the gas in the gap, the particular radiation capable of producing thermoluminescence is absent. Similarly, in the case of the spark discharge, it could be assumed that there is present, either one radiation capable of producing both effects, or else two radiations, one producing ionization and the other thermoluminescence.

While the evidence available is not sufficient to establish either of these suggestions (which are only put forward tentatively as showing that the absence of thermoluminescence in the case of the silent discharge does not necessarily imply the absence of entladungstrahlen), it is interesting to note that different types of spark discharge give rise to entladungstrahlen of various intensities. For example, the entladungstrahlen emitted from an "intense" spark are found to be more penetrating than those emitted from a "thin" spark of equal length. A penetrating type is also emitted from the lengthened spark discharge produced at a pressure of only one or two millimetres of mercury *, and it has been observed that entladungstrahlen are also emitted from the luminous parts of the discharge in a vacuum tube. [As far as the writer is aware, it does not seem to have been investigated whether or not they are emitted from a silent discharge at ordinary pressure.] From this it seems reasonable to expect that the conditions under which the

* See Phys. Rev. 1909, xxviii. (Mar.) p. 225.

discharge takes place should influence the type of radiation emitted, in the sense that while radiations from all types of discharge might produce ionization, only the wave-lengths emitted from particular types could produce thermo-luminescent effects. Further work on the radiation in this region would probably give interesting results in this connexion.

Summarizing the results of the experiments as a whole, it may be stated that:

(1) Before the three-point phenomenon can be obtained, some form of discharge, silent or spark, must be "visible" from the main gap, and within a certain distance of it.

(2) The phenomenon is obtained in the absence of

(*a*) disturbances of the electric field near the main gap, and

(*b*) the passage of ions from the pilot discharge into the main gap.

(3) A radiation is emitted by the pilot discharge, which can ionize the gas in the main gap.

(4) When this radiation is prevented from reaching the main gap, the usual three-point effect is not obtained.

(5) The three-point effect is still produced when the electrodes are so shielded as to prevent any photo-electric effects being shielded by the radiation.

(6) The observed properties of this radiation seem to establish the limits of its wave-length as being approximately 1000 Å. and 13 Å., and they coincide to a large extent with the corresponding properties of entladungstrahlen.

It is therefore inferred that the three-point effect is caused by the ionization of the gas in the main gap by a radiation, believed to be a form of entladungstrahlen, emitted by the pilot discharge. Disturbances of the field, passage of ions into the gap, or photo-electric effects produced by the radiation or by ultra-violet light, while possibly assisting in, are not essential for, the production of the three-point effect. (It is interesting to note that when the radiation is prevented from reaching the gap by means of a quartz plate, photo-electric effects at the electrodes due to ultra-violet light emitted from an intense pilot discharge and transmitted by the plate, may give rise to a diminished form of three point effect. Under these conditions, of course, the ultra-violet light is the main cause of the effect.)

If the radiation proves to be a form of entladungstrahlen, two interesting facts are disclosed regarding it.

(1) That entladungstrahlen are produced in air at ordinary pressure by a silent discharge as well as by a spark.

(2) That a critically adjusted spark gap subjected to impulsive voltages forms a convenient indicator of the presence of entladungstrahlen (when no other radiations are present which ionize gases or produce photo-electric effects), and that it appears to be more sensitive in use than either an ionization chamber or a thermoluminescent salt.

Incidentally, it is suggested that possibly either or both of the modified types of three-point gap used in this work might, on investigation, prove to be more suitable as a standard type of gap than the usual type employed, in which an insulated pointed third electrode is used.

In conclusion, the writer desires to thank Dr. Taylor Jones for the interest he took in the work and the suggestions he made during the progress of of it. The experimental part of the work was carried out in the Physical Laboratory of the University College of North Wales, Bangor.

XXIX. *On the best Linear Relation connecting Three Variables.* *By* F. J. W. Whipple *.

1. THE choice of the best linear relations connecting any number of variables was the subject of a paper published† in the 'Philosophical Magazine' by Professor Karl Pearson in 1901. Approaching the question from a geometrical standpoint, Pearson gave his paper the title "The Lines and Plans of closest Fit to Systems of Points in Space." A "supplementary" paper was published recently ‡ by Professor H. S. Uhler, "Determination of the Minimum Plane in Four-Dimensional Space with respect to a System of Non-Coplanar Points." This was followed § in the next issue of the 'Philosophical Magazine' by a paper by Mr. H. Glauert, "The Determination of the best Linear Relationship connecting any Number of Variables." This last communication appears to have been written without knowledge of Pearson's work.

In all these three papers the criterion by which best fit is defined is the same. The plane or line of best fit is such that the sum of the squares of the perpendiculars from the

* Communicated by the Author.
† Phil. Mag. (6) ii. p. 559 (1901).
‡ Phil. Mag. (6) xlix. p. 1260 (June 1925).
§ Phil. Mag. (6) l. p. 250 (July 1925).

points in question on to that plane or line is a minimum. Now, when other variables are represented by the coordinates of points, the question of scale assumes great importance. If the scale on which one variable is represented is doubled, so that one coordinate (say, x) of each of the representative points is doubled, the new plane of closest fit will not be related in any simple way to the old one. In so far as Professor Uhler deals with the geometrical representation of statistics, he says that his variables "are treated as having equal mathematical weights." Mr. Glauert is more explicit. He makes the assumption that the variables involved in the analysis fall into two classes, one subject to errors of observation and the other known accurately. He assumes that if there had been no errors of observation the variables would have satisfied exactly an equation of the first degree. Moreover, he assumes that, for each of the variables which are subject to errors of observation, the probable magnitude of an error is the same.

In most statistical problems these assumptions could not be justified. There is no *a priori* reason to anticipate that the variables satisfy an equation of the first degree exactly. What we wish to obtain is an equation of the first degree which is the best available as an indication of the type of interdependence of the variables. Glauert's second assumption is really an instruction * to choose the units for the several variables so that the probable errors will have the same numerical value. There is no general method available for the selection of such units. To select units so as to give the "standard deviations" of the variables from their mean values the same numerical value is a device well known to meteorologists through the work of Mr. W. H. Dines; it does not meet Mr. Glauert's requirements, but it has the advantage of making the choice of units depend on the nature of the variations under investigation rather than on such an accident as the accuracy with which they can be measured. For example, two investigators may be dealing with a problem in which temperature has to be measured over a range of 50° C. One investigator considers that his temperatures have a probable error of 1° C., the other claims that his probable error is 0°·1 C. With Glauert's criterion the results of the two observers should be plotted on different scales, and the linear relations arrived at when temperature

* That this is also Prof. Uhler's meaning can be seen by reference to his paper, "Method of Least Squares and Curve Fitting," Journal of the Optical Society of America and Review of Scientific Instruments, vol. vii. no. 11, p. 1043 (1923).

is correlated with other variables will be quite different. With Dines's criterion the scales will be the same and the results the same for the two observers.

2. As has been mentioned, the problem which presents itself in statistical inquiries is to obtain the equation of the first degree which is the best available as an approximate relation between the variables. To define more precisely what is meant by "best" in this connexion we must use symbols. To simplify matters we consider only * the case of three variables.

Let x_1, x_2, x_3 be the departures of the three variables from their mean values.

Let a, b, c, be three undetermined coefficients, and let

$$ax_1 + bx_2 + cx_3 = \epsilon. \quad . \quad . \quad . \quad . \quad (1)$$

If the variables x_1, x_2, x_3 had been uncorrelated, then each of the expressions

$$\Sigma x_2 x_3,\ \Sigma x_1 x_3,\ \Sigma x_1 x_2$$

would have been zero (the summation denoted by Σ extending over all the observed values of x_1, x_2, and x_3). In that case $\Sigma\epsilon^2$ would have been equal to

$$a^2\Sigma x_1^2 + b^2\Sigma x_2^2 + c^2\Sigma x_3^2.$$

It is reasonable to say that the equation,

$$ax_1 + bx_2 + cx_3 = \epsilon,$$

is the best available representation of the relation between the variables, if a, b, c are so chosen that $\Sigma\epsilon^2$ bears as small a ratio as possible to

$$a^2\Sigma x_1^2 + b^2\Sigma x_2^2 + c^2\Sigma x_3^2.$$

This definition has the advantage that it is independent of the units in terms of which the variables are measured. If x_1, x_2, x_3 are multiplied by constant factors, then the best fitting linear relation is determined consistently by the straightforward algebraic transformation.

3. Let us write

$$\lambda = \frac{\Sigma(ax_1 + bx_2 + cx_3)^2}{a^2\Sigma x_1^2 + b^2\Sigma x_2^2 + c^2\Sigma x_3^2}. \quad . \quad . \quad . \quad (2)$$

* The somewhat trivial case of two variables is dealt with below, p. 384.

Since λ is to be a minimum for variations of a, it follows that

$$\lambda a\Sigma x_1^2 = a\Sigma x_1^2 + b\Sigma x_1x_2 + c\Sigma x_1x_3. \quad . \quad . \quad . \quad (3)$$

If the number of "observations" is n, the standard deviations σ and the correlation coefficients r are defined by equations such as

$$n\sigma_1^2 = \Sigma x_1^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$nr_{12}\sigma_1\sigma_2 = \Sigma x_1x_2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Accordingly, equation (3) may be written

$$\lambda a\sigma_1 = a\sigma_1 + br_{12}\sigma_2 + cr_{13}\sigma_3. \quad . \quad . \quad . \quad . \quad (6)$$

In the same way the conditions for λ to be a minimum for variations of b and c may be written down, so that we have the three equations

$$\left.\begin{aligned} (1-\lambda)a\sigma_1 + r_{12}b\sigma_2 + r_{13}c\sigma_3 &= 0, \\ r_{12}a\sigma_1 + (1-\lambda)b\sigma_2 + r_{23}c\sigma_3 &= 0, \\ r_{13}a\sigma_1 + r_{23}b\sigma_2 + (1-\lambda)c\sigma_3 &= 0. \end{aligned}\right\} \quad . \quad . \quad . \quad (7)$$

By elimination of a, b, c, we find that

$$\begin{vmatrix} 1-\lambda, & r_{12}, & r_{13} \\ r_{12}, & 1-\lambda, & r_{23} \\ r_{13}, & r_{23}, & 1-\lambda \end{vmatrix} = 0. \quad . \quad . \quad . \quad (8)$$

The parameter λ is the least positive root of this equation. When λ has been determined the ratios of the coefficients a, b, c are given by the equations of the preceding group.

4. Since the condition $\lambda = 1$ would indicate complete independence of the variables, whilst the condition $\lambda = 0$ would indicate that they satisfied exactly an equation of the first degree, it is appropriate to call $1-\lambda$ the coefficient of mutual correlation and to denote it by a symbol R_{123}. When there is no risk of confusion the suffixes may be omitted.

It will be seen that the coefficient of mutual correlation is the greatest root of the equation,

$$\begin{vmatrix} R, & r_{12}, & r_{13} \\ r_{12}, & R, & r_{23} \\ r_{13}, & r_{23}, & R \end{vmatrix} = 0. \quad . \quad . \quad . \quad (9)$$

When a, b, c have the values given by (7) the equation

$$ax_1+bx_2+cx_3=\epsilon \quad . \quad . \quad . \quad . \quad . \quad (10)$$

may be called the mutual regression equation. It can be written

$$\begin{vmatrix} x_1/\sigma_1, & x_2/\sigma_2, & x_3/\sigma_3 \\ r_{12}, & \mathrm{R}_{123}, & r_{23} \\ r_{13}, & r_{23}, & \mathrm{R}_{123} \end{vmatrix} = \epsilon. \quad . \quad . \quad (11)$$

An alternative form is

$$\frac{x_1}{\sigma_1}(\mathrm{R}_{123}{}^2-r_{23}{}^2)^{\frac{1}{2}} \pm \frac{x_2}{\sigma_2}(\mathrm{R}_{123}{}^2-r_{13}{}^2)^{\frac{1}{2}} \pm \frac{x_3}{\sigma_3}(\mathrm{R}_{123}{}^2-r_{12}{}^2)^{\frac{1}{2}} = \epsilon. \quad (12)$$

This form is more symmetrical, but it suffers from the drawback that the signs to be attributed to the radicals have to be determined by comparison with equations such as (11).

The criterion adopted—namely, that $\Sigma\epsilon^2$ should bear as small a ratio as possible to $a^2\Sigma x_1{}^2+b^2\Sigma x_2{}^2+c^2\Sigma x_3{}^2$—has led to the same linear equation as would have been arrived at by regarding the variables as coordinates, plotted on such scales that each of the three standard deviations was represented by the unit of length, and finding the plane of closest fit.

5. In equations (10) and (11) the right-hand side is written as ϵ, not as zero. This is an indication that the variables do not satisfy exactly the equations which would result from the substitution of 0 for ϵ. It is useful, however, to have the equations written in such a way that the magnitude of the departure from zero is indicated. This can be done by introducing * the symbol Ca to signify a "casual" number, the standard value of which, *i. e.*, the square root of the mean value of the square, is unity.

In this way we can write (10) in the form

$$\frac{ax_1+bx_2+cx_3}{(a^2\sigma_1{}^2+b^2\sigma_2{}^2+c^2\sigma_3{}^2)^{\frac{1}{2}}} = (1-\mathrm{R})^{\frac{1}{2}}\,\mathrm{Ca}. \quad . \quad . \quad (13)$$

Similarly, in place of (12) we have the equation

$$\frac{\frac{x_1}{\sigma_1}(\mathrm{R}^2-r_{23}{}^2)^{\frac{1}{2}} \pm \frac{x_2}{\sigma_2}(\mathrm{R}^2-r_{13}{}^2)^{\frac{1}{2}} \pm \frac{x_3}{\sigma_3}(\mathrm{R}^2-r_{12}{}^2)^{\frac{1}{2}}}{(3\mathrm{R}^2-r_{23}{}^2-r_{13}{}^2-r_{12}{}^2)^{\frac{1}{2}}} = (1-\mathrm{R})^{\frac{1}{2}}\,\mathrm{Ca}. \quad . \quad (14)$$

It will be noticed that in the very special case in which

* 'Royal Meteorological Society, Quarterly Journal,' l. p. 237 (1924).

R_{123} is unity, the three ordinary regression equations, such as

$$\begin{vmatrix} x_1/\sigma_1, & r_{12}, & r_{13} \\ x_2/\sigma_2, & 1, & r_{23} \\ x_3/\sigma_3 & r_{23}, & 1 \end{vmatrix} = (1-r_{23}^2)^{\frac{1}{2}} \begin{vmatrix} 1, & r_{12}, & r_{13} \\ r_{12}, & 1, & r_{23} \\ r_{13}, & r_{23}, & 1 \end{vmatrix} \text{Ca}$$

are all equivalent to each other and to the mutual regression equation,

The casual number, or residual, determined by equation (14), is correlated, of course, with x_1, x_2, and x_3. If $r_{1.123}$ is the correlation coefficient for the residual and x, then

$$r_{1.123}^2 = \frac{(1-R)(R^2-r_{23}^2)}{3R^2-r_{23}^2-r_{13}^3-r_{12}^2}, \quad . \quad . \quad . \quad (15)$$

and it follows that

$$r_{1.123}^2 + r_{2.123}^2 + r_{3.123}^2 = 1-R. \quad . \quad . \quad . \quad (16)$$

6. The special cases, in which two of the three correlation coefficients r_{12}, r_{13}, r_{23} are equal, are of interest.

If $r_{12}=r_{13}<r_{23}$ and r_{23} is positive, then the greatest root of the equation in R

$$\begin{vmatrix} R, & r_{12}, & r_{13} \\ r_{12}, & R, & r_{23} \\ r_{13}, & r_{23}, & R \end{vmatrix} = 0$$

is equal to r_{23}. In this case the mutual regression equation (14) reduces to

$$\frac{1}{\sqrt{2}}\left[\frac{x_2}{\sigma_2} - \frac{x_3}{\sigma_3}\right) = (1-r_{23})^{\frac{1}{2}} \text{Ca}. \quad . \quad . \quad . \quad (17)$$

and does not contain x_1 at all.

On the other hand, if $r_{12}=r_{13}>r_{23}$ and r_{23} is positive, then r_{23} is the smallest root of the critical equation instead of the largest.

The equation reduces to

$$(R-r_{23})(R^2+r_{23}R-2r_{12}^2)=0, \quad . \quad . \quad . \quad (18)$$

and the greatest root is given by

$$R=\tfrac{1}{2}[(r_{23}^2+8r_{12}^2)^{\frac{1}{2}}-r_{23}]. \quad . \quad . \quad . \quad . \quad (19)$$

Finally, if r_{23} is negative and $r_{12}=r_{13}$, then (19) gives the only positive root of the critical equation.

In either of these last two cases the mutual regression

equation is of the symmetrical form

$$a\cdot\frac{x}{\sigma_1}-\frac{y}{\sigma_2}-\frac{z}{\sigma_3}=\epsilon, \quad . \quad . \quad . \quad . \quad . \quad (20)$$

with $$a=\frac{r_{12}(\mathrm{R}-r_{23})}{r_{12}^2-r_{23}\mathrm{R}}.$$

The three cases in which $r_{12}=-r_{13}$ can be dealt with in the same way.

7. It is a question of practical importance whether the mutual regression equation represents a real addition to knowledge. It will do so if the mutual correlation coefficient is considerably greater than any of the correlation coefficients for the pairs of variables. In the extreme case in which R is unity the three coefficients are related like the cosines of three angles whose sum is 360°. For instance, with $r_{12}=r_{13}=r_{23}=-\frac{1}{2}$, the mutual regression coefficient is unity and the mutual regression equation may be written

$$\frac{x_1}{\sigma_1}+\frac{x_2}{\sigma_2}+\frac{x_3}{\sigma_3}=0 \text{ Ca.}$$

In general, for R to be much greater than the numerical value of any of the three r's, the product of these three must be negative.

When the three variables x_1, x_2, x_3 are regarded as co-ordinates of points in three-dimensional space we can entertain the possibilities that the points may have a spindle-like distribution or a disk-like distribution. In the former case a straight line is a good approximate representation, in the latter a plane. Such a plane is defined by the mutual regression equation. The range of utility of mutual regression equations is indicated by the geometrical illustration.

8. *Note on the Correlation of Two Variables.*

With two variables the mutual correlation coefficient is numerically equal to the ordinary correlation coefficient, as may be seen from the fact that in the case of two variables the analogue of equation (9) is $\mathrm{R}^2-r_{12}^2=0$. The mutual regression equation for two variables is

$$\frac{1}{\sqrt{2}}\left(\frac{x_1}{\sigma_1}\mp\frac{x_2}{\sigma_2}\right)=(1\mp r_{12})^{\frac{1}{2}}\,\mathrm{Ca},$$

the upper sign of the ambiguities being taken if r_{12} is positive, the lower if it is negative.

XXX. *On the Separation of Crystalloids from one another by Dialysis.* *By* Louis Kahlenberg, *Ph.D., Professor of Chemistry, University of Wisconsin**.

Introduction.

ON the basis of the data which Thomas Graham † collected in his classical experiments on osmosis and dialysis, he classified substances into crystalloids and colloids. The crystalloids were crystalline bodies which he had found passed through animal bladder or parchment. On the other hand, non-crystalline or glue-like bodies he found did not go through the membranes he employed, and to these bodies he gave the name colloids. Ever since Graham's time it has been held that crystalline substances go through membranes, and non-crystalline substances (*i.e.* colloids) do not. While Graham's experiments were fundamental and important, the data which he collected at that early time were limited in number. Moreover, he used relatively few solutions and tested them with but few membranes, so that, while his deductions were quite in harmony with his experimental observations, the latter were far too limited in number to afford a sufficiently broad basis of induction for such general conclusions as he drew, and as have been held by scientists and expounded in text-books during all of the decades since Graham's time.

The fact is that crystalline substances can very well be separated from one another by dialysis. All that is necessary is to select suitable membranes and solutions to accomplish this. Indeed, it is even quite possible to separate "crystalloids" from "colloids" by having the "*colloids*" *pass through* the membrane and the "*crystalloids*" *remain behind,* if the proper septum and the proper solvent be employed. To complete the statement of the situation, one can also separate "colloids" from "colloids" by dialysis, by choosing the proper solvent and membrane. In my experimental researches "On the nature of the process of Osmosis and Osmotic Pressure with observations concerning Dialysis" ‡, specific examples of each of these cases are given.

* Communicated by the Author.

† Philosophical Transactions, cli. part 1, p. 183 (1861); also Phil. Mag. (4) xxiii. p. 204 (1862).

‡ 'Journal of Physical Chemistry,' x. pp. 144–209 (1906); also Trans. Wis. Acad. Sci., Arts, & Letters, xiv. part 1.

The purpose of the present investigation is to present additional cases of separation of crystalloids from one another by dialysis in non-aqueous solutions, and to show that such separations can also be accomplished in aqueous solutions. Up to the present time, the separation of crystalloids from one another by dialysis in aqueous solutions has offered peculiar experimental difficulties. Indeed, such separations have commonly been regarded as impossible, though it is well known to physiologists that processes of this kind actually take place continually in plants and animals as they live. It was the experimental study of dialysis in non-aqueous solutions that suggested the line of attack to obtain similar results with aqueous solutions.

Experimental.

(a) *Non-aqueous Solutions.*

In the dialysis of non-aqueous solutions a rubber membrane, vulcanized caoutchouc, was employed. This membrane was of the sheet-rubber or so-called rubber-dam material commonly used by dentists. It was found to be fairly uniform and pliable. It could readily be stretched over the mouth of a thistle tube and secured perfectly by means of windings of stout cotton thread. The area of the membrane obtained by thus tying the sheet-rubber over the mouth of the thistle tube was about 5 sq. cm., while the capacity of the bell of the thistle tube was 50 c.c. Twenty-five cubic centimetres of the solution to be dialysed were placed in the tube so prepared, and the latter was then immersed in the pure solvent so that the level of the liquid in the outer dish was about the same as that in the tube.

After testing the action of a large number of liquids on rubber, it was found that pyridine was by far the most suitable one for the dialysis experiments. Water, of course, could not be used, for, not being absorbed by rubber, no osmotic action occurred. Alcohol, being but slightly absorbed by rubber, gave a little action, but it was entirely too slow. Hydrocarbons and their halogen substitution products did very well, but they soon softened the rubber so greatly that the membrane became distended, smeary, and too weak. Esters, ketones, aldehydes, and nitriles also proved to be unsuitable, acting too slowly or exerting too great a solvent action and consequently disintegrating the

rubber. On the other hand, pyridine is readily imbibed by rubber without appreciably weakening, disintegrating, or even unduly distending the rubber membrane. Indeed, sheet-rubber soaked by pyridine may be freed from the latter by wringing the liquid out as one would wring water from a cloth. The rubber when then hung out on a line will "dry" much the same as will a cloth that has been wet with water.

Pyridine will dissolve a great variety of substances. One would naturally expect this, for it is miscible in all proportions with water on the one hand, and also with practically all organic solvents on the other hand. Thus many substances dissolve in pyridine which are also soluble in hydrocarbons. Such substances invariably pass through rubber membranes in dialysis experiments,* for rubber itself is practically a hydrocarbon in nature. On the other hand, pyridine also dissolves certain substances that are soluble in water but not soluble in hydrocarbons; and such substances do *not* pass through rubber membranes. So, for example, sulphur, naphthalene, and camphor dissolve in pyridine. They are also soluble in hydrocarbons, therefore in rubber, and they consequently all pass through rubber membranes upon dialysis. Again, silver nitrate, lithium chloride, and cane-sugar are soluble in pyridine but not in hydrocarbons, therefore not in rubber, and consequently they do not pass through rubber membranes. From these facts one would conclude that the following substances may be separated from each other by dialysis in pyridine solutions using rubber membranes, the substance first named in the case of each pair passing through the membrane:—Sulphur from sugar; naphthalene from sugar; sulphur from silver nitrate; naphthalene from silver nitrate; camphor from sugar; camphor from silver nitrate; sulphur from lithium chloride; camphor from lithium chloride; naphthalene from lithium chloride. It was actually found in the laboratory that these separations can be made by means of dialysis as above described. The solutions used contained 1·5 per cent. of each of the substances in question. The dialysis proceeded quite normally, the length of time required to secure practically complete separation varying from two days to three weeks. When rather thin membranes were used and the outer liquid was renewed every two or three hours, the time required to effect the separation was materially shortened.

* Compare Kahlenberg, Journ. Phys. Chem. x. p. 141 (1906).

(b) *Aqueous Solutions.*

Among the precipitated membranes, first devised by Moritz Traube * and employed by Pfeffer † in his osmotic investigations, the copper ferrocyanide membrane was perhaps the most successful one. It is well known that this membrane is practically impervious to sugar. On the other hand, quite a number of other substances will pass through this septum. Urea, for instance, will pass through fairly readily. It ought, therefore, to be possible to separate sugar from urea by means of a copper ferrocyanide membrane. Such was actually found to be the case. A copper ferrocyanide membrane was formed in a good quality of thin parchment paper that was tied over the mouth of a tube by means of stout thread. Great care had to be exercised in securing the membrane properly, and indeed it was only after a number of trials that a membrane free from leaks was finally obtained. The copper ferrocyanide precipitate was formed in the membrane in the usual way; namely, by first soaking the parchment in water so as to eliminate air-pockets, and then placing a 5-per-cent. solution of copper sulphate on one side of the paper and a solution of potassium ferrocyanide of about the same concentration on the other. After several hours' standing these solutions were removed, the membrane well rinsed with water, and the dialysis begun.

The solution in the dialyser contained 2 grams of sucrose and 2 grams of urea in 100 c.c. The outer liquid was pure water. The area of the membrane was about 100 sq. cm. For a period of five days *urea only* passed out of the dialyser, showing that sugar and urea were actually being separated from each other by dialysis. The outer liquid was continually renewed in an effort to remove all of the urea from the solution. Thus far it has not been possible to accomplish this without some of the sugar also passing through the membrane after five to ten days. In other words, the membrane became defective after that time. The fact that such membranes are apt to become leaky after being in use for a time has also been observed by others. During these experiments it was found that not only sucrose, but also maltose, lactose, galactose, dextrose, and lævulose do not pass through copper ferrocyanide membranes. The observations were confirmed with four different and quite perfect membranes. Urea, on the other

* *Archiv. für Anat. u. Physiol.* p. 87 (1867).
† *Osmotische Untersuchungen*, Leipzig (1877).

hand passed through all of these membranes. My thanks are due to Mr. H. D. Baernstein for help in carrying out the experiments with the copper ferrocyanide membranes.

Lanoline, the fat of the wool of the sheep, is known to be able to absorb more than 50 per cent. of its weight of water. It occurred to me that this hydrated lanoline would probably exhibit selective osmotic properties, and such, indeed, proved to be the case. A very large amount of time and labour had to be expended in finding a satisfactory method of preparing osmotic membranes of lanoline. In this work my assistant, Dr. John R. Koch, and my son, Dr. Herman H. Kahlenberg, were especiallly helpful in the laboratory. With their aid and enthusiasm it was possible to carry out a very large number of experiments that finally yielded good results.

In order to produce osmotic membranes of lanoline, the latter had to be absorbed in suitable inert supporting material. As such materials, fine muslin, linen, silk, copper gauze, and parchment paper were tried. These materials were tied over the mouth of a tube and then soaked in molten lanoline, care being taken in this process to get rid of occluded air. The difficulty arose in getting perfectly uniform and sufficiently thin membranes that were quite free from flaws. If the membranes were too thick, their action was slow ; on the other hand, the effort to secure thin membranes naturally frequently resulted in getting defective ones. After many trials, it was found that a fine quality of China silk and a good, rather thin, parchment paper were the best materials in which to absorb the lanoline to obtain good working membranes. In tying the material over the mouth of a tube, silk was, of course, much better than parchment, for the stiffness of the latter made it more difficult to secure it to the glass without leaks. On the other hand, when parchment bags were used, this difficulty was obviated, and excellent, quite thin membranes were obtained. In the present research, membranes of silk impregnated with lanoline were used. After carefully tying the silk over the mouth of the thistle tube, the silk was dipped in molten lanoline and moved about in the latter so as to get rid of air-bubbles. The tube was then removed from the lanoline bath and held near a flame so that the excess of lanoline ran off. In this process the tube should be slowly rotated and manipulated so as to secure as even a distribution of the lanoline in the silk as possible. By careful manipulation and repeated dipping of the membrane, if necessary, satisfactory, continuous films of lanoline in the

silk fabric may be obtained. Gross leaks in such membranes could be detected by simply filling the tube with water and suspending it in the air for a while, when the water would drip from the membrane if the latter was very defective. However, the absence of such dripping was by no means proof that the membrane was sufficiently tight for osmotic experiments. By filling the tube with Congo red solution and immersing it in water, it was found that the membrane was generally tight if none of the dyestuff appeared in the outer liquid. However, this test also was not absolutely reliable, for if any salts were dissolved in the water to which the Congo red had been added, the latter was frequently precipitated, and consequently did not make its way through the membrane in spite of the fact that it was not absolutely free from leaks. A solution of cane sugar, or one of nickel chloride, was found best as a means of testing the membranes. If these solutions did not pass through, the membrane was quite tight.

It should be remarked here that, besides preparing lanoline membranes by imbibing that fat in materials like silk, parchment, etc., as stated above, the attempt was made to impregnate collodion membranes with lanoline, or to deposite a film of the latter on the inner side of a collodion sack. The attempts to dissolve lanoline in collodion or to add the former to collodion solutions by first dissolving the lanoline in a solvent like ether, alcohol, carbon disulphide, acetone, petroleum ether, carbon tetrachloride, various esters, etc., and then adding this solution to the collodion, practically always failed to give satisfactory films. The membranes were either entirely too weak, or it was not possible to peel them from the glass tube or other vessel in which they had been formed. Attempts to form the sacks in porcelain or metallic dishes yielded no better results. A large amount of time was spent in efforts to secure a good osmotic membrane by this means, and in the course of this work many substances were tried. It was found that on the whole the best membranes were obtained when the lanoline was dissolved in chloroform and then added to the collodion, or when the collodion sack was first formed in the test tube or other glass vessel in the usual way, and then, just before peeling the sack out, a chloroform solution of lanoline was poured in so as to completely fill the sack and then carefully poured out again. In this way a film of lanoline was deposited on the inner side of the collodion sack which could be removed from the glass tube as usual after the smell of chloroform had

practically disappeared. Solvents other than chloroform yielded films that were not continuous, thus resulting in leaky membranes. The amount of time and care that had to be spent in thus securing perfect membranes by depositing a lanoline film on collodion was so great, and the advantage of these membranes over those obtained by soaking silk or parchment in lanoline was so small, that the collodion-lanoline membranes were not used in the final tests. On the other hand, however, it was found that by dipping silk or parchment in chloroform solutions of lanoline, very good and quite thin membranes were obtained, and such membranes were actually used with good success in this laboratory. The solution used in forming the membranes was prepared by dissolving 100 grams of lanoline in 250 c.c. of chloroform. The attempts to substitute other solvents for chloroform resulted in membranes that were leaky, weak, or otherwise poorer in quality for osmotic experiments.

Thistle tubes, over the mouth of which silk impregnated with lanoline was secured as already described, were used in the following experiments. The bell of each thistle tube had a capacity of about 50 c.c. In each case 25 c.c. of the solution to be tested was carefully poured in by means of a capillary funnel tube, and the thistle tube so charged was immersed in a small beaker in 130 c.c. of water, the water in and outside of the dialyser being arranged so as to be on the same level. A large number of dialysers were prepared. In fact, during the progress of the experiments frequently between seventy and one hundred dialysers were in operation at one time. In each case the results obtained were carefully checked by duplicate or triplicate experiments to make sure that the observations were not due to faulty septa.

Five-per-cent. solutions of each of the following substances were placed separately in dialysers as described: boric acid, borax, sodium chloride, sodium sulphate, Rochelle salt, magnesium sulphate, urea, cane-sugar, dextrose, lactose, egg albumin, litmus, fuchsine. Of these substances, urea, sodium chloride, boric acid, and borax passed through the lanoline membranes fastest. In three days quite appreciable amounts were found in the respective outer liquids. In an equal time, mere traces of sodium sulphate and magnesium sulphate had passed through their respective dialysers. Cane-sugar, lactose, and dextrose did not pass through at all, not even after two weeks. During the latter period of time only traces of Rochelle salt had passed through. Egg

albumin did not pass through, and traces of litmus appeared in the outer liquid only after eight days. No fuchsine was present in the outer liquid till after ten days, while after three weeks only 0·04 per cent. of the total fuschine has passed out of the dialyser as determined colorimetrically. These results were corroborated by means of similar lanoline membranes prepared by dipping the silk in a solution of lanoline in chloroform. With the latter membranes it further was found that of the various acids tested, boric acid passed through fastest*. In two days large quantities of boric acid had passed through the septum, whereas it required seven days for hydrochloric acid to pass through perceptibly. Acetic and sulphuric acids were still slower than hydrochloric acid. Citric and tannic acids passed in mere traces after 25 days, and oxalic acid did not pass through, even after 45 days.

Borax † passed through fairly rapidly, but not as fast as boric acid. In three days common salt came through in abundance. Potassium chloride and potassium iodide also passed through fairly rapidly as compared with other salts. However, Rochelle salt, sodium sulphate, potassium nitrate, and copper sulphate appeared in the outer liquid only in small quantities, even after ten days. Nickel chloride, sodium acetate, silver nitrate, magnesium sulphate, lithium chloride, ferric chloride, and potassium alum did not pass through, even after six weeks. Again, leucine, cystine, egg albumin, amino butyric acid, phenyl alanine, tyrosine, alanine, glutamic acid hydrochloride, lactose, dextrose, sucrose, mannose, galactose, fructose, and formic aldehyde did not pass through, even after six weeks of continued dialysis. Substances of a pronouncedly alkaline character attacked the membrane strongly, causing leaks, and then, of course, went through the passage formed. This was true of sodium carbonate, potassium carbonate, potassium cyanide, sodium cyanide, sodium silicate, and soap. Even 1-per-cent. solutions of these went through rapidly because of the disintegration which they had caused. Potassium permanganate in 5-per-cent. solutions decomposed the membrane in a few hours. A 1-per-cent. solution did not pass through in six weeks; but this was doubtless because the permanganate was reduced, forming

* It is remarkable that boric acid has also been found to pass through the living human skin. Compare Kahlenberg, Journ. Biological Chem. lxii. p. 159 (1924).

† Borax does not pass through the living skin. See Kahlenberg, *loc. cit.*

insoluble manganese hydroxide. Potassium nitrate and potassium chlorate passed through slightly in two weeks, potassium chromate in four days, while potassium bichromate did not pass, even after four weeks. Of all of the organic compounds tested, *urea passed through the membrane most rapidly.* Only slight traces of ethyl alcohol passed through after six weeks, glycerin required ten days to make its appearance in the outer liquid, while methylene blue did not go through the membrane at all.

The facts above presented suggest the possibility of making a large number of separations of crystalloids from each other by dialysis. It has been found that such separations are not always easy to make, especially if it is desired to make complete separations ; for in some cases the presence of an additional substance in solution influences the permeability of the membrane for the substances concerned. A number of separations have been made completely, and the following may be reported at this time :—

Urea from mannose. The urea passed through and was removed completely. The mannose did not appear till after 31 days, when the membrane became slightly defective. The solution contained 5 per cent. of each substance to begin with. The lanoline was absorbed in silk in this experiment.

Sodium chloride was separated from nickel chloride. The experiment lasted seven days ; 5 per cent. of each salt was present in the solution when dialysis was started. In this case lanoline was absorbed in thin parchment paper.

Similarly, urea was separated from sodium chloride, the former passing through so much more rapidly that the separation was practically complete in four days.

Boric acid was separated from sucrose by dialysis. In this case, too, parchment paper was used as a backing for the membrane. The experiment lasted five days.

The separations took considerable time, for the membranes acted slowly, it having been necessary to make them sufficiently thick so that they would not develop flaws during the process of dialysis.

What is there in lanoline that gives it these wonderful, selective osmotic properties? This question naturally presents itself. Lanoline is distinguished from other fats particularly by the fact that it is very rich in cholesterine.

It was therefore indicated that cholesterine was probably the active selective ingredient. This actually proved to be the case, as was definitely demonstrated by experiments

that were carried out in collaboration with my son, Dr. Herman H. Kahlenberg. The details of these investigations will soon be ready for publication. It should be stated here, however, that not only does cholesterine possess these selective osmotic properties, but phytosterine, the analogous non-saponifiable ingredient of plant oils, also shows practically the same properties. Since cholesterine is present in all living animal cells, it would seem likely that *it is extremely delicate films of these sterenes that give living cells their wonderfully selective osmotic properties.* Moreover, since animal oils contain cholesterine and all plant oils similarly contain phytosterine, one would naturally expect membranes made of such oils to exhibit selective osmotic properties to some degree, especially when relatively considerable amounts of these sterenes are present. This, too, has been found to be the case*. In working out the latter fact Mr. Clarence Hrubesky, one of my assistants, has been very helpful. In preparing large quantities of pure cholesterine a number of my students have helped in the laboratory. The result has been that not only have osmotic membranes been made of these sterenes, but the latter have been carefully studied as to their physical and chemical properties. Finally, in the further separation of crystalloids by dialysis with sterene membranes, my assistant, Dr. John R. Koch, acted as collaborator in the experimental work. The results of these further researches will soon be ready for publication.

Madison, Wisconsin.
October 1925.

* Attempts have been made to prepare osmotic membranes from materials other than lanoline or sterenes by means of the methods above described. Beeswax was tried, but was found to be perfectly inactive and impervious to all aqueous solutions as long as the septum was intact. It was found that camphor, borneol, alpha-naphthalene or beta-naphthalene, when dissolved in the various solvents mentioned above, yielded no continuous films that could be used in osmotic experiments. Furthermore, when each of these substances was dissolved in molten beeswax, lanoline, or tallow and then the resulting mass dissolved in chloroform, carbon tetrachloride, ether, ether plus alchol, petroleum ether, or carbon bisulphide, no continuous films could be produced except when lanoline was used. The presence of the latter in any membrane always resulted in osmotic action.

XXXI. *The Air-Bubble Viscometer.*

By Guy Barr, *B.A., D.Sc.* *

[Plate VI.]

Summary.

(*a*) It was desired to find whether, and under what circumstances, the rise of a large bubble in a vertical tube containing liquid could be used as an indication of the viscosity of the liquid.

(*b*) The effects of length of bubble and diameter of tube have been examined and the rate of rise determined for several oils of known viscosity and surface tension, for water and for glycerin in different tubes. A dimensional analysis of the problem has been made involving certain assumptions which seem to be capable of verification, in any particular case, from the appearance of the bubble.

(*c*) Above a certain limit the length of the bubble is without appreciable effect on the rate of rise. For bubbles rising "slowly" in a given tube, *i.e.* at such a rate that not more than one thickened annulus of liquid appears between the bubble and the walls towards the rear end of the bubble, it has been found that the rate of rise is inversely proportional to the kinematic viscosity, provided that the surface tension is constant. An approximate determination has been made of the form of the function of r/a upon which, in addition to the viscosity, the rate of rise depends. In certain conditions, *e.g.* when light oils are examined in a tube of such a diameter as to give a convenient rate of rise, the rate may vary about fourteen times as fast as the diameter and six times as fast as the surface tension, but these effects become very much less pronounced when viscous liquids are used in wide tubes.

(*d*) The air-bubble viscometer may be used with confidence for the approximate comparison of viscosities of materials of the same class. A simple modification is suggested which enables a check to be made on the assumed constancy of surface tension.

Introduction.

ONE of the oldest works methods of obtaining an idea of the viscosity of liquid is probably that developed in the apparatus of Cochius, in which a tube nearly full of the liquid is inverted, and the time taken by the more or less cylindrical air-bubble to travel over a certain distance is noted. The Cochius instrument itself has been largely used in the nitro-cellulose industry, and simple forms are much used in varnish making. A short examination of the

* Communicated by the Author. Published by permission of the Aeronautical Research Committee.

influence of diameter of tube and length of bubble on the rate of rise has been published by Faust (*Zeits. Phys. Chem.* xciii. p. 758, 1919), who used a very viscous oil for his experiments. An elaboration stated to be suitable for use with oils having viscosities varying from 0·15 to 0·9 poise has been described by Abrams, Kavanagh, and Osmond (Chem. and Met. Eng. xxv. p. 665, 1921). Gardner and Holdt (Circ. No. 128 of Paint Manufacturers' Association of the U.S., 1921) advance suggestions for the application of the method in varnish works, involving the use of a set of standard tubes containing oils of known viscosity from about 0·5 to 5·5 poises, the viscosity of the sample being estimated from that of the standard which gives most nearly the same rate of rise. None of these authors appear to have recognized that the surface-tension of the liquid must, at least in some circumstances, play a part in determining the rate of rise of the bubble. This influence will be discussed later.

A number of experiments have been made in connexion with this type of viscometer in order to obtain some idea of the limitations to which it is subject.

Influence of size of Bubble and Tube.

The effects of length of bubble and of diameter of the tube were first investigated in the case of water, and in this series it was decided to avoid, as far as possible, errors due to variation in cross-section of the tube at different points. With this end in view, the time required for the flow of 100 c.c. of water past the bubble was measured, the velocity being adjusted by suitable variation of the head so that the bubble remained practically stationary in the vertical tube instead of rising as in the case of the Cochius or Abrams viscometer. The water was taken from the mains, and its temperature varied by only negligible amounts throughout the series. Care was taken to adjust the velocity of flow towards the end of a run so that the surface of the bubble returned exactly to the original position. The times observed were fairly concordant, varying by 1·5 per cent. as a maximum (except in the smallest tube, where the differences amounted to 10 per cent.) : in general about four determinations were made, so that the means are probably subject to an error of not more than 0·3 per cent. The diameters of the tubes were subsequently measured by weighing the mercury which filled a length of some 10 cm. in the neighbourhood of the bubble. The following table contains the results given by three

tubes; it was not found possible to keep a bubble stationary in a tube of diameter 0·58 cm.

Diameter of tube.	Length of bubble.	Mean time required to collect 100 c.c.
0·633 cm.		308 secs.
0·652 „	2·2 cm.	225·3 „
	5·1 „	226·2 „
	16·2 „	225·1 „
1·00 „	1·0 „	20·1 „
	2·0 „	19·4 „
	5·5 „	19·2 „
	12·0 „	19·4 „

Although this table clearly demonstrates that the diameter of the tube has a very large effect on the rate of flow of water past the bubble, the deliveries do not vary even approximately as the fourth powers of the diameters as was found by Faust for his oils : the product, time of flow of 100 c.c. × (diameter of tube)^4, amounts for the three tubes to 49·6, 40·6, and 19·3 respectively. His conclusion as to the absence of any effect due to length of bubble is, however, confirmed by these experiments, at any rate for bubbles having a length greater than the diameter of the tube.

Relation between Rate of Rise and Viscosity.

In a second series, tubes were set up as viscometers of the Cochius type: marks were etched 10 cm. apart and each about 7 cm. from the end of the tube. One end of the tube was sealed and the other end closed, after introduction of the liquid to be used, by a well-fitting glass rod and rubber tubing. The viscometer tube was fixed into the corks at either end of a water-jacket of which the temperature could be adjusted electrically. By means of two sets of levelling screws on a brass plate attached to the water-jacket it was possible to arrange that the tube should be vertical whichever end was uppermost when the screw-points rested on a suitably shaped horizontal plate, and that no further adjustment should be necessary after inversion. The temperature was kept constant at 25° C. It was again verified that the length of the bubble was without appreciable influence on the results, and, except where otherwise stated, a length of about 2·5 cm. was used.

When the diameter of the tube was 0·478 cm., water gave times of rise of the bubble through 10 cm. which varied very considerably *e. g.* from 103 to 182 secs. ; a 2·5-cm. bubble gave a mean time (mean of 14) of 147 secs., a 1·2-cm. bubble a mean time of 136 secs. A glycerin solution of sp. gr. 1·02 (viscosity about 1·2 centipoises) gave a time 1283 secs. With oils much better concordance was obtained, and duplicates agreed generally within 1 per cent. The following figures were obtained :—

Oil.	Viscosity.	Time of rise of bubble.	$\frac{\text{Viscosity}}{\text{time of rise}} = (1)$.	$\frac{(1)}{\text{density}}$.
Singer	0·144 poise	27·3 secs.	0·00528	0·00622
Machine.....	0·609 ,,	107·7 ,,	0·00565	0·00636
Dynamo.....	3·07 ,,	496·0 ,,	0·00612	0·00660

In a tube of diameter 0·652 cm. the following observations were made, the duplicates being again accordant :—

Liquid.	Viscosity.	Time of rise.	$\frac{\text{Viscosity}}{\text{time of rise}} = (2)$.	$\frac{(2)}{\text{density}}$.
Machine oil.	0·609	4·4 secs.	0·138	0·155
Dynamo ,,	3·07	18·6 ,,	0·165	0·178
Castor ,,	6·51	41·0 ,,	0·159	0·166
Glycerol ...	6·31	55·6 ,,	0·113	0·090

The viscosities given in the second column were determined by an absolute method and by means of calibrated Ostwald tubes (Rep. and Mem. of Aeronautical Research Committee, No. 906, 1923).

Though a rough proportionality between the viscosity and time of rise is apparent in either of the above tables, there are variations of 15 to 40 per cent. in the "constants" of column 4. The variations are not systematic, *i. e.* the constant does not increase regularly with the viscosity ; nor is any improvement effected by making the obvious replacement of viscosity by kinematic viscosity as has been done in the last column. From the fact that the most marked discrepancy occurs between the figures for glycerol and for the oils in the second table, it seems possible that the surface-tension may be of importance, since glycerol has a surface-tension considerably different from that of oils.

Theoretical.

Dimensional analysis of the problem leads to equations such as

$$v = \frac{d^2\rho g}{\eta} \cdot f\left(\frac{d^2\rho g}{\mathrm{T}}, \frac{d^3\rho^2 g}{\eta^2}, \frac{l}{d}\right), \quad . \quad . \quad . \quad (1)$$

where

v is the linear velocity of rise of the bubble ;
l „ length of the bubble ;
d „ diameter of the tube ;
ρ, η, and T are the apparent density (in air), the viscosity and the surface-tension of the liquid ;
g is the acceleration due to gravity.

In this form the equation is of little assistance, but we may introduce certain limitations which render it more simple. For the type of motion with which we are dealing, it has been shown that the length of the bubble is without influence on the velocity, so that we may neglect l/d in the function in brackets. It is also clear, from the experiments, that to a first approximation $v \propto \frac{l}{\eta}$, so that the kinetic energy terms are unimportant ; the function $\frac{d^3\rho^2 g}{\eta^2}$ is, in fact, convertible to Reynolds's criterion by multiplying it by $\frac{\eta v}{d^2\rho g}$, so that if the motion be sufficiently slow, this function may be regarded as a constant, from analogy with the laws of ordinary viscous flow. Hence it appears reasonable to inquire whether the simplified formula

$$v = \frac{d^2\rho g}{\eta} f\left(\frac{d^2\rho g}{\mathrm{T}}\right) \quad . \quad . \quad . \quad . \quad . \quad (2)$$

will accord with the experimental facts.

The function $f\left(\frac{d^2\rho g}{\mathrm{T}}\right)$ which occurs on the right-hand side will be more readily recognized in the form $\phi\left(\frac{r}{a}\right)$, which is more usually employed in surface-tension problems, to which it is equivalent since $\mathrm{T} = 1/2a^2\rho g$, where a^2 is the specific cohesion. The function is thus related to the shape of the portion of the bubble concerned, *i. e.* of the rear end. Faust's measurements on two very viscous oils indicate that in tubes of 1·6 to 2·4 cm. diameter the linear velocity is very nearly proportional to d^2, decreasing only by some 2 to 5 per cent. more than it should for strict proportionality. He

gives no measurements of the surface-tension, but at room temperatures most mineral oils have a value of about 0·267 cm. for a, so that r/a in these cases lies between about 3·0 and 4·5. The decrease in velocity below that required by the relation $v \propto d^2$ becomes more marked in the smaller tubes; it amounts to 13 per cent. in his smallest tube of diameter 1·2 cm., for which, assuming the above value of a, the ratio r/a was 2·3.

With the smaller values of r/a which occur in the measurements recorded above for four different oils, the function by which $\frac{d^2\rho g}{\eta}$ has to be multiplied to give the observed velocity of rise is found to be much smaller. In this connexion the surface-tensions of the oils in question and of the sample of glycerol used were measured by the drop-weight method, using the precautions and factors indicated by Harkins and Humphrey J. Am. Chem. Soc. xxxviii. 228, 1916 and xli. 518, 1919; the values obtained for the $\sqrt{\text{specific cohesion}}$ at 25° C. were

	a.	$\frac{0{\cdot}652}{2a}$.	$\frac{0{\cdot}478}{2a}$.
Singer oil	0·265	—	0·90
Machine ,,	0·266	1·22	0·90
Dynamo ,,	0·272	1·20	0·88
Castor ,,	0·281	1·16	—
Glycerol ...	0·325	1·03	—

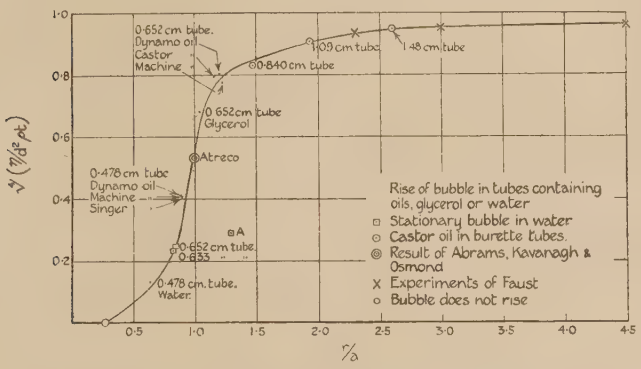
The values of r/a in these experiments thus extend from 0·88 to 1·22, and it is obvious from the experimental results that the value of $f\left(\frac{d^2\rho g}{\mathrm{T}}\right)$ increases very rapidly with r/a. Thus the "constants" (viscosity/time of rise) for the two tubes, taking the figures for machine oil and dynamo oil, are related, not as d^2, but roughly as $d^2 \times (d^2)^{4\cdot15}$.

The values obtained experimentally for $\sqrt[4]{\frac{\eta}{d^2\rho t}}$ (where t is the time required for the bubble to rise 10 cm.), *i. e.* for $\sqrt[4]{\left(\frac{\eta v}{d^2\rho g} \cdot \frac{g}{10}\right)}$, have been plotted against r/a in the accompanying diagram (fig. 1), the fourth root being used merely for convenience in reducing the scale. Corresponding values have been deduced from the experiments with the

stationary bubble in water. In order to get an idea of the form of the curve over a larger range of r/a, the following further observations were made :—

(*a*) In a tube of small enough diameter containing liquid a bubble is found not to rise at all ; possibly there might be a slow rise if the walls were perfectly wetted, but this would appear to be infinitely slow. The limiting value of r/a was deduced approximately by using acetone, benzene, chloroform, water, etc. in tubes of various sizes, as about 0·27 ; but the exact limit seems to depend on other factors, so that this figure may be in error, for a particular liquid, by say $\pm 0{\cdot}04$.

Fig. 1.


0·652 cm tube. Dynamo oil Castor Machine
1·09 cm tube
1·48 cm tube
0·840 cm tube
0·652 cm tube Glycerol
Atreco
0·478 cm tube Dynamo oil Machine Singer
A
0·652 cm tube. 0·833 "
0·478 cm. tube. Water.
Rise of bubble in tubes containing oils, glycerol or water
□ Stationary bubble in water
○ Castor oil in burette tubes.
◎ Result of Abrams, Kavanagh & Osmond
X Experiments of Faust
○ Bubble does not rise
$\sqrt[4]{(\eta/d^2\rho t)}$
r/a

(*b*) Faust's results, already quoted, indicate that the curve becomes practically horizontal at high values of r/a, the function here plotted increasing by some 2·1 per cent. between $r/a=2{\cdot}3$ and $r/a=3{\cdot}0$, and by only 1 per cent. between $r/a=3{\cdot}0$ and $r/a=4{\cdot}5$. The gap between these figures and those above recorded was bridged by some rough determinations, at "room" temperature, of the rate of rise of bubbles in burette tubes of diameters 0·840, 1·096, and 1·41 cm. containing castor oil ; the viscosity of the castor oil at the prevailing temperature was deduced from the known Redwood times by Higgins's formula, using temperature coefficients derived from Kahlbaum and Räber's table; the value for a was taken as 0·285 cm. The points so found are indicated by circles. After drawing a smooth curve through the whole of the points obtained, the curve was extrapolated by identifying the value of $\sqrt[4]{\left(\frac{\eta}{d^2rt}\right)}$ for the oil used by Faust at $r/a=2{\cdot}3$ with that given by the curve,

and calculating the corresponding values indicated by his results for $r/a = 3{\cdot}0$ and $r/a = 4{\cdot}5$.

The point marked Atreco is derived from the statement by Abrams, Kavanagh, and Osmond (*loc. cit.*) that the factor to convert to "Saybolt seconds" the times of rise of the bubble in the bubble viscometer described by them is approximately 10, the factor increasing with the viscosity if the diameter of the tube is more than 0·53 cm., and decreasing with the viscosity if the diameter is less than 0·52 cm. Applying the Saybolt conversion formula $\eta/\rho = 0{\cdot}00213t - 1{\cdot}535/t$ to any one of the oils mentioned by them as used for calibration, and assuming the factor 10 to be correct for a diameter of 0·525 cm., the value of an ordinate may be deduced corresponding with a value of r/a of 0·99, where a is taken as 0·265 cm. for the temperature of 100° F. at which they worked. The point is found to agree well with the curve; the closeness of the agreement must be regarded as somewhat fortuitous in view of the assumptions necessary.

The position of the point A, which represents the rate of rise of a bubble in water in a 1-cm. diameter tube, may serve as a reminder of the limitations we have introduced into the dimensional method. When the viscosity of the liquid is low and the rate of rise high, due to the use of a wide tube, *i. e.* to the existence of a fairly high ratio of r/a, there is an obvious change in the form of the bubble, especially at its lower end. For the slowest movements (viscous liquids with $r/a < 1{\cdot}1$, or mobile liquids with $r/a < 0{\cdot}7$) the two ends of the cylindrical bubble appear roughly hemispherical, the thickness of the film of liquid on the walls being otherwise uniform from top to bottom, as far as can be seen. As the rate of rise increases, owing either to reduction in viscosity or increase in r/a, the top of the bubble becomes more elongated (bullet-nosed) and the rear end more flattened; the flattening of the rear end is accompanied by the development of a short neck at about 1 diameter length above its lowest point, where the thickness of the film on the wall is several times as great as either just above or just below; this stage is illustrated in figs. 2 A and B (Pl. VI.). This neck becomes gradually longer as the velocity of the bubble is increased (*cf.* fig. 2 C): about this stage, kinetic energy terms may presumably begin to form an appreciable fraction of the viscous losses. At still higher velocities the change of curvature may appear at 3 or 4 diameters above the bottom of the bubble, and the relative increase in thickness of the film becomes less. In a slightly wider tube the thickened

film itself breaks up into one or more further thickened rings with thinner layers between them; such a stage is illustrated in fig. 2 D, corresponding with point A, where, however, the full number of rings cannot be distinguished as well as by visual examination of the bubble. In a tube of say 2 cm. diameter containing water the bubble shows no thickening of the film, but it is obvious that the motion is no longer steady, for the flattened base of the bubble does not remain symmetrical about the axis of the tube.

This last observation is interesting as being the extreme indication of the labile nature of the phenomenon discussed. Anyone who has noticed the rise of a bubble in a tube will have recognized that the steady flow, occurring when the tube is vertical, is metastable, the rate of rise increasing very rapidly for small deviations from the vertical. The apparent stability is conditioned by the viscous damping forces; and when these are reduced by increasing the diameter of the tube the system reverts to its normally unstable state where the thickness of the liquid film is not uniform round the circumference and the viscous resistance offered is less than for the uniform film.

The more complicated conditions of flow which occur when the kinetic energy terms are not negligible are reflected in the fuller dimensional formula

$$v = \frac{d^2\rho g}{\eta}\, f\left(\frac{d^2\rho g}{\mathrm{T}},\ \frac{d^3\rho^2 g}{\eta^2},\ \frac{l}{d}\right). \qquad (1)$$

This formula indicates at once that the flow is not fixed solely by the value of r/a, but that the function also involves kinetic energy terms and possibly also the ratio of l to d.

Conclusion.

There is a very large number of "practical" cases in which the viscosity (of a lubricating oil or of a varnish for example) does not require to be known more accurately than to some 5–10 per cent. The above measurements and theoretical discussion show that so long as there is a close concordance between the surface-tensions of the liquids compared, and the diameter of the tube selected is such as to give a suitably slow rate of rise, the time required for the bubble to travel over a given distance is proportional, within an error of less than this amount, to the kinematic viscosity. The comparison of viscosities is least affected by surface-tension when the viscosities are so high that wide tubes may be employed, such that the value of r/a is above about 2·0. If it is desired to make use of the method for

liquids of lower viscosity (0·2 to 5 poises), it is necessary to recognize that very serious error may be occasioned by a small difference in surface-tension (see below). For liquids of viscosity less than, say, 0·1 poise the scheme is quite unsuitable, particularly when, as with aqueous solutions, the surface-tension is high and may be greatly depressed by impurities to an extent depending on the rate of absorption of solute at the air-liquid interface; with such low viscosities the diameter of the tube necessary to secure the required slow rate of rise becomes so small that unavoidable variations of diameter are liable to render the rise irregular owing to their large effect on the ratio r/a. In works and other places where one type of liquid only is handled, it may frequently be sufficient to assume that the surface-tension remains constant. But it will generally be more satisfactory to supplement the "viscosity" determination by a comparison of the surface-tensions, which may readily be carried out on the same sample of liquid if the bubble tube be provided with a capillary tip so that the number of drops corresponding with the volume contained between the fiducial marks may be counted. The external diameter of the capillary should be in accordance with the suggestions of Harkins and Humphrey (*loc. cit.*), *e.g.* about 0·55 cm. for oils such as those used above, and its length and internal diameter such as to cause the drops to be formed not faster than, say, one per 10 secs.

The curve illustrates well the enormous effect of the diameter of the tube upon the rate of rise of the bubble under certain conditions. For tubes of the diameter used by Abrams, Kavanagh, and Osmond (*loc. cit.*) with oils having $a = 0{\cdot}265$ cm., the relative time of rise of the bubble is indicated as decreasing some twelve to fifteen times as fast as the relative increase in diameter *. Since the

* In the neighbourhood of $r/a = 1{\cdot}0$ the curve approximates to a straight line having the equation $\sqrt[4]{\left(\frac{\eta}{d^2\rho t}\right)} = \mathrm{K}\left(\frac{r}{a} - c\right)$, where K and c have numerical values about 2 and 0·7 respectively. Hence $\frac{dt}{t} = -\frac{2(3\frac{r}{a} - c)}{\frac{r}{a} - c}\frac{dr}{r}$, and assuming $\frac{r}{a} = 1$ and $c = 0{\cdot}7$, we have $dt/t = -15\,dr/r$ at this point. Similarly when r is constant, $\frac{dt}{t} = \frac{4\frac{r}{a}}{\frac{r}{a} - c}\cdot\frac{da}{a}$, so that, taking the above values for r/a and c, $\frac{dt}{t} = 13{\cdot}3\frac{da}{a}$. Hence $\frac{dt}{t} = 6{\cdot}6\frac{d\Gamma}{\Gamma}$.

diameter was only 0·525 cm., this would mean that a variation in diameter of 0·001 cm. would change the time of rise of a bubble by some 2·5 per cent. It is thus of little use to specify the viscosity by stating a certain time of rise in a tube of specified diameter in this range, but each tube should be calibrated by means of suitable standard liquids of appropriate viscosity.

The effect of differences in surface-tension on the rate of rise of a bubble in a tube of fixed diameter may also be very large. With oils in the "Atreco" viscometer the percentage change in rate of rise (*i. e.*, in indicated viscosity) may be some six or seven times the percentage change in surface-tension. The effect is shown to diminish very rapidly with increase in diameter of the tube, *i. e.* when the viscosity of the liquid examined is so high as to allow such an increase to be made without unduly increasing the velocity.

Gardner and Holdt (*loc. cit.*) do not give details sufficient to allow their results to be interpreted on the curve here obtained ; but since their viscosity range is higher and their tubes wider, it would seem that dt/t is only about three times as great as dr/r : they suggest that dr/r should be not more than 5 per cent. to give the reproducibility at which they aim, which is presumably not better than ± 15 per cent. in view of the rapid rise with which they appear to work. In these wide tubes the surface-tension is relatively unimportant.

XXXII. *The Production of some Spectra of Carbon, Oxygen, and Nitrogen in the Presence of Neon.* *By* W. H. B. Cameron, *M.Sc., Research Student, Queen's University Belfast* *.

A NUMBER of recent papers have described modifications of spectra produced by admixture of substances with the inert gases, and in this respect the action of Helium was particularly notable. In connexion with Carbon † spectra there is the production of the Comet-Tail bands and of the Negative Carbon bands with great intensity, the isolation of the Triplet System, and under other conditions, of the arc lines of Carbon. More recently Merton and Pilley ‡ have demonstrated a strong development of the

* Communicated by Dr. R. C. Johnson, B.A., Ph.D.

† Proc. Roy. Soc. A. ciii. p. 383 (1923); & cviii. p. 343 (1925).

‡ Phil. Mag. [6] l. p. 195 (1925); Proc. Roy. Soc. A. cvii. p. 411 (1925).

Negative bands of Nitrogen, and have also isolated the arc lines of this element in high-pressure Helium. A year ago, an investigation was made by Dr. Johnson and myself of the action of Argon on spectra *. The present communication describes similar work in connexion with Neon.

The Effect of Neon on Carbon Spectra.

Swan bands and Triplet System.—The discharge-tubes which were used in this investigation were of the usual H pattern, having a bore of about 15 mm., each being furnished with carbon electrodes, quartz window, palladium regulator, and side bulbs containing caustic potash and phosphorus pentoxide. A charcoal trap immersed in liquid air was employed to purify the neon. In view of the action of both helium and argon in developing the Swan bands rather than the Angström bands when carbon is present as an impurity, it was not surprising to find that neon behaved in a similar manner, and that on admitting hydrogen, the Triplet System was isolated as in the case of the two inert gases mentioned.

Comet-Tail bands.—The production of the comet-tail bands in high-pressure helium, a phenomenon which has no counterpart in the case of argon, has already been noted, and steps were taken to ascertain whether neon was capable of producing this spectrum. A discharge-tube containing neon at a pressure of 25 mm. was run for a considerable time in order to reduce the quantity of carbon present. After several hours the glow began to assume the red colour of neon and striæ appeared along the tube. When examined with the spectroscope, this showed the neon lines and the comet-tail bands. Their isolation from the other familiar band spectra of carbon in the visible region was complete. This development of the system was not as intense as that in helium but was equally definite. The band in the red at λλ 6246, 6196 was present precisely as in helium, though somewhat confused in this case with the strong neon lines in the neighbourhood. A system of bands associated with the comet-tail bands is recorded by Johnson in a recent paper (Proc. Roy. Soc. A. cviii. p. 350, 1925), and Birge † has shown that these two systems are numerically related. These bands are produced also, though rather faintly, along with the cometary bands in neon. It is perhaps worth

* Proc. Roy. Soc. A. cvi. p. 195 (1924); Phil. Mag. [6] xlviii. p 1069 (1924).

† 'Nature,' Aug. 8, 1925, p. 207.

mentioning that in a wide-bore tube with aluminium electrodes having less than 1 mm. of neon and only a very minute quantity of carbon, the comet-tail bands were faintly visible.

Carbon line spectrum.—When tubes in the above condition were subjected to a mild condensed discharge they glowed with a brilliant yellow light. Analysis showed that the greater part of this light came from neon lines, but that the cometary bands persisted faintly. A search was made for the carbon arc lines which appear under similar conditions in helium, but with the exception of λ2478 no trace of these could be found. Some of the doublets of C.II. were present.

Negative Carbon bands.—The great intensity of the negative carbon bands was a striking feature of their development in helium. In neon at similar pressures this system appeared with moderate strength together with the 3rd positive bands o carbon greatly reduced in intensity and traces of the 4th positive bands. A condensed discharge practically eliminated the 3rd and 4th positive bands leaving the negative bands outstanding, provided only a small quantity of carbon was present.

The CH bands.—An interesting observation was made in the case of a tube containing only a minute trace of carbon and high-pressure neon. A photograph taken on a quartz prism spectrograph revealed, along with faint traces of the comet-tail bands and the Swan head λ 5165 a strong development of the CH band λ 4315 and associated heads. The only other prominent features were the OH bands which appeared with moderate intensity. In every case in which the isolation of the CH band from other carbon spectra was effected, the OH bands occurred also. The tube could not have contained much hydrogen as the Balmer series was but faintly visible.

Martin's CS bands.—Some of the tubes which were filled with high-pressure neon presumably contained as an impurity a minute trace of sulphur. When these were in the condition described above, and were showing the CH band, they also showed Martin's CS bands quite well defined, From the conditions under which this system was observed, it would seem that its appearance furnishes the most sensitive test of the presence of sulphur if there exists also a trace of a carbon impurity (which is always difficult to eliminate). Both these phenomena could be produced equally well in high-pressure argon.

A new band system associated with Carbon.—An additional system of bands has been observed when uncondensed

discharges are used to excite wide-bore tubes having the usual accessory bulbs and filled with high-pressure neon. (The discharge-tubes were fitted with carbon electrodes.) These bands could not be obtained with very great intensity even with exposures of six hours. In Table I. measurements of some thirteen heads are given. Other heads were

TABLE I.

Intensity.	Wave-length. (I.A.)	Intensity.	Wave-length. (I.A.)	
0	2257·7	0	2451·8	
0	2259·5	1	2453·9	
0	2260·3	2	2455·0	*a*
0	2261·2	2	2456·0	
—	—	1	2457·8	
0	2277·0	—	—	
0	2278·5	1	2492·9	
0	2279·6	1	2494·4	
0	2280·5	1	2495·7	
—	—	1	2497·5	
0	2369·0	0	2510·9	
0	2371·2	1	2513·7	
1	2372·2	2	2514·9	
1	2373·3	2	2516·2	
0	2375·0	1	2517·8	
1	2388·8	0	2531·9	
1	2391·1	1	2534·5	
2	2392·1	2	2535·6	
2	2393·1	—	2536·7	*b*
1	2394·8	1	2538·6	
1	2409·2	0	2553·3	
1	2411·4	1	2555·9	
2	2412·5	2	2557·1	
2	2413·5	2	2558·2	
1	2415·3	1	2560·2	
0	2430·3	0	2575·3	
0	2432·4	3	2577·7	
1	2433·4	2	2579·1	
1	2434·5	2	2580 2	
0	2436·2	1	2582·2	

a=doubtful, possibly fine structure work.
b=confused with the mercury line.
Other members of the system are present, but confused with structure of the third positive Carbon bands.

visible, but were too much confused with the 3rd positive carbon bands to render their measurement under this dispersion of much value. The band system as a whole is of the usual type and degraded to the red; each "head" has a somewhat complex structure embracing five sub-heads. The system was found under conditions in which the Swan bands, the

comet-tail bands, or the Triplet System appeared in the visible region, and a weak development of the negative carbon bands invariably accompanied the system. With the present available evidence, however, it is difficult to assign it to any particular molecule. It is believed that this band spectrum has not hitherto been recorded. The same bands have also been observed in helium and argon, but only very faintly.

Neon-Oxygen Mixtures.

In view of recent work by McLennan and Shrum* describing the production of the green aurora line in helium-oxygen and neon-oxygen mixtures, a special search has been made for this line under various discharge conditions. We have examined neon-oxygen mixtures of varying composition and pressure with both uncondensed and condensed discharges and in wide and narrow bore capillary discharge-tubes, but have been unable to find any trace whatever of this line. The only explanation we are prepared to offer is that possibly heavier currents are needed for its production, and we never used more than 5–10 amps. through the primary of the induction coil.

Oxygen band spectra.—It has been found possible to develop weakly the band spectra of oxygen with mild condensed discharges through wide-bore tubes in the presence of neon at all pressures up to 25 mm. The intensity of the ultra-violet emission bands, attributed by Johnson† to an O_2 molecule, relative to that of the negative bands when produced in neon, is greater than in the normal production of these systems by condensed discharges through pure oxygen.

Line spectrum O.I.—In the case of wide-bore discharge-tubes, uncondensed discharges gave practically no light whatever proportions of neon and oxygen were used. Very long exposures, of course, ultimately gave the principal lines of both gases. Attention is therefore confined to condensed discharges in the case of wide-bore tubes.

With a little neon, say 1 mm., the addition of a small quantity of oxygen gave only the first members of the series of O.I. Increasing the pressure of neon up to 5 or 6 mm. gave practically no change, but neon at 25 mm. pressure had the effect of extending considerably the several series of oxygen. In the case of capillary tubes a little neon together with various quantities of oxygen brought up P(2), P(3), $p(2)$, $d(4)$, fairly strongly. Increasing the proportion of oxygen

* Proc. Roy. Soc. A. cviii. p. 501 (1925).
† Proc. Roy. Soc. A. cv. p. 683 (1924).

seemed to effect a slight reduction in the intensity of $d(4)$ under all conditions of discharge. The uncondensed discharge through a capillary tube containing high-pressure neon extended the series and, in particular, excited the higher members of the sharp and diffuse triplet series. When condensed discharges are passed through capillary tubes, the most energetic type of excitation results. In the presence of a little neon (say 1 mm.) to which oxygen was added, the most notable effect of adding more oxygen was to increase the intensity of the principal singlet series while the sharp and diffuse triplets got weaker. With 5 mm. of neon addition of oxygen produced practically no change excepting a slight enhancement of $p(2)$. Similarly, if the oxygen content is fixed and the neon content varied, there results little change over the range 0 to 5 mm., but high-pressure neon develops the higher members of the series well,—especially the sharp and diffuse triplets. Table II. includes most of these facts.

Table II.

Discharge Conditions and Bore.	Neon content.	Oxygen content.	Results.
Condensed. Wide Bore.	1 mm.	Small quantity.	Only first members visible.
	5 mm.	do.	Practically no change.
	25 mm.	do.	Series considerably extended.
Uncondensed. Capillary.	1 mm.	A little.	P (2), P (3), p (2), d (4) fairly strong.
	5 mm.	do.	d (4) slightly reduced, otherwise no change.
	25 mm.	do.	Higher members of Sharp & Diffuse triplets strong.
Condensed. Capillary.	1 mm.	A little.	Fairly good development of series lines. Principal Singlets enhanced; Sharp & Diffuse Singlets & Triplets reduced as above.
	5 mm.	do.	No change except slight enhancement of p (2).
	25 mm.	do.	Higher members much better developed, especially Sharp & Diffuse Triplets.

It is noteworthy that a mild condensed discharge through a wide-bore tube containing high-pressure neon and a little oxygen gives the best development of the higher members of the series in O.I. At all pressures of neon a condensed discharge is capable of bringing up the stronger members of the elementary series of oxygen in addition to the lines of the compound or series spectrum.

Neon-Nitrogen Mixtures.

The recent work of Merton and Pilley (*loc. cit.*) on the spectra of helium-nitrogen mixtures disclosed some interesting features. As the partial pressure of nitrogen was diminished, a stage was reached when the first and second positive band spectra disappeared and the negative bands remained, developed strongly along the whole tube. The system as thus produced was considerably extended towards the red,—a feature apparently characteristic of the production of several band spectra in helium. Similar phenomena to these have been observed in the case of nitrogen in neon, and with a trace of the former in high-pressure neon the negative nitrogen bands can be isolated with intensity. When a mild condensed discharge is passed through a tube in this condition, it yields a spectrum consisting of the neon lines and some arc lines of nitrogen. Not all the arc lines of nitrogen isolated in helium are produced in high-pressure neon. Some lines recorded by Merton and Pilley as very strong do not seem to be present, but quite a number of the arc lines of nitrogen have been identified and measured. With the comparatively small dispersion of the prism spectrograph used, it is possible that a few lines of nitrogen really present were confused with strong neon lines. Table III. gives a list of all the nitrogen arc lines identified

TABLE III.

Nitrogen arc lines.	Intensity in Helium.	Intensity in Neon.	Nitrogen arc lines.	Intensity in Helium.	Intensity in Neon.
6874·3	1	1	4305·5	6	3 d
6653·5	4	4	4253·3	3	2
6484·9	8	4	4230·4	4	3
4935·0	9	4	4223·1	5	3
4914·9	4	1	4215·0	—	3
4750·2	2	2	4137·6	4	3
4492·4	5	2 d	4113·9	5	2
4358·3	7	2	4099·9	9	9
4336·5	4	7	4011·0	4	1
4317·7	4	2	4000·0	3	1
4313·1	3	2 d			

d = diffuse.

by the complete measurement of a single plate taken under the above conditions. None of the spark lines of nitrogen were visible. The intensities of such arc lines as appear are in many cases in agreement with those of Merton and Pilley for the lines in helium. There are, however, some intensity

changes too obvious to admit of any doubt, and there are many strong lines attributed to nitrogen which we have not been able to produce in our experiments with nitrogen-neon mixtures. On the other hand, there are a number of lines which we have been unable to identify as arising from impurities, and it seems just possible that they may belong to the arc spectrum of nitrogen. The approximate measurements of these, as far as we have determined them roughly from one plate, are :—

6992·5 (5) ; 6425·1 (2) ; 6004·7 (3) ;
4216·1 (4) ; 4024·6 (2) ;

In the event of any theoretical work pointing to this origin it should be possible to measure these up accurately.

Discussion.

We have now available for the first time, data relating to the production of some spectra of carbon, oxygen, and nitrogen in all three inert gases, viz., helium, neon, and argon, and a discussion of their comparative behaviours would not seem superfluous. For the sake of clearness a summary of these data is presented in Table IV.

TABLE IV.

System.	In Helium.	In Neon.	In Argon.
Comet-Tail bands.	Strong.	Less strong.	Absent.
Associated bands.	Fairly strong.	Weak.	Absent.
Negative C bands.	Very strong.	Moderately strong.	Very weak.
Carbon arc lines.	Present.	Absent.	Absent.
Negative N bands.	Strong.	Strong.	Absent.
Nitrogen arc lines.	Present.	Present in part.	Absent.
Triplet System.	Present.	Present.	Present.
Ultra-violet Oxygen bands.	Weak.	Weak.	Absent.
Negative Oxygen bands.	Fairly strong.	Very weak.	Absent.
O.I.	Present.	Present.	Present.
O.II.	?	Strong members present.	Absent.

In the paper of Merton and Pilley already mentioned, the authors put forward an interesting suggestion to explain the phenomena of the development of certain arc spectra in

the inert gases. Briefly expressed, the theory states that the presence of any inert gas in large excess increases the expectation of life of the neutral atom from which the spectrum arises, and at the same time allows the passage of a heavy current. Added to these effects there is a limit placed by the resonance potential of the inert gas used to the energy which may be acquired by the bombarding electrons during the passage of a condensed discharge. The critical potentials of helium, neon, and argon are as follows :—

Gas.	*Resonance.*	*Ionization.*	*Author.*
He.....	20·4 21·2	25·6 25·3	Franck & Knipping
Ne.....	11·8 17·8	21·5	Hertz.
A	11·5	15·1	Horton & Davies.

The nitrogen arc lines appear well in helium, some appear in neon, but they are absent in argon. In accordance with the above theory this would suggest that the excitation potential of the N.I. spectrum lies in the neighbourhood of 11·8 volts. The lines of N.II. are not found in the presence of any of these inert gases, and consequently this excitation potential must lie above 20·4 volts This is in agreement with Miss Payne's estimated value of 24 volts for the second ionization potential of nitrogen, after the first electron has been removed.

In the case of carbon line spectra difficulties present themselves. The carbon arc lines appear in helium only, but some of the spark lines are unmistakably present in both helium* and neon. The first difficulty is connected with the non-appearance of the arc lines of carbon in neon when it is remembered that some spark lines appear. Moreover, Saunders has suggested that the first ionization potential of the neutral carbon atom may be 7 or 8 volts, and this would allow of the production of the arc lines in all three inert gases. The second difficulty arises when we attempt to explain the presence of such spark lines as do appear. The highest energy level to which the second electron must be raised in order to radiate the lines observed in helium is the 5 (ϕ) level. This would require a 22·1 volts† impact on an *ionized* carbon atom, which is clearly disallowed by the above theory.

* Proc. Roy. Soc. A. cviii. p. 343 (1925).

† Calculated from Fowler's value for the series limit : Proc. Roy Soc. **A. cv.** p. 299 (1924).

As regards the first problem mentioned, any explanation at the present time must be of a very speculative nature. It is suggested that the manner of breaking down of the molecule which contains the carbon atom and the potential at which this occurs are of more fundamental importance than the actual excitation potentials of the line spectra. Thus at the comparatively low voltages obtainable in neon the compound may break down and yield as one of the products only *ionized* carbon atoms, which are then available as sources of the spark spectrum, and at higher voltages such as may be obtainable in helium only it may break down in a different manner yielding in addition neutral carbon atoms from which arises the arc spectrum. Before applying to the case of nitrogen for which some data are available, a further suggestion will be made which may help to elucidate the second difficulty pointed out. Examination of a plate showing the carbon arc lines developed in the presence of high-pressure helium revealed the fact that the complete arc spectrum of the inert gas was produced. The significance of this is obvious. While it is admitted that the probability of a *free* electron acquiring energy above the first resonance level of helium is very remote, it is clear that the electrons in many helium atoms must be raised to much higher energy levels. This is probably due to secondary collisions and to "photo-impact." It seems reasonable to assume that these excited helium atoms may impart their energy to carbon atoms if such are in the neighbourhood, so that the latter may be excited up to the *ionization* level of helium. The same reasoning would hold in the case of the other inert gases. Under particularly energetic conditions it may be possible to exceed this limit. This was proved in the case of high-pressure argon in a capillary bore tube, excited by a heavy condensed discharge, when the blue spectrum of argon was developed. It was interesting to note that some of the carbon-spark doublets appeared faintly under these conditions.

On this modification of Merton and Pilley's view,—viz., that under moderate discharge conditions energy up to the first ionization potential is available, and under more energetic conditions even above this limit,—it is possible to explain in some degree most of the phenomena recorded above. Since the ionization potential of C.II. is 24·3 volts and that of helium and neon 25·6 and 21·5 respectively, it should be possible to develop the spark spectrum of carbon completely in helium and partially in neon provided ionized carbon atoms are present. In helium, all the doublets above

λλ 2746, 2747 have been recorded with the exception of that at λ4267, and the majority of the remaining members are in the extreme ultra-violet. It still remains to be explained, however, why some of the pairs whose radiation is energetically possible do not occur in the presence of helium. In neon the same C.II. lines are recorded as in helium with the possible exception of λ 2992, at which position there is a neon line. This is unfortunate, as the fact of the presence or absence of this C. II. line would be a test of the truth of the above assumption, since its excitation potential is 22·1 volts. All the lines which do occur have excitation potentials below the ionization potential of neon.

Reverting to the case of nitrogen, we note that Smyth* has found critical potentials for this molecule at 16·9, 24·1, and 27·7 volts, which he interprets as corresponding to the changes :

$$N_2 \rightarrow N_2^+ ; \quad N_2 \rightarrow N^{++} + N \text{ or } N_2 \rightarrow N^{++} + N^- ; \quad N_2 \rightarrow N^+ + N^+$$

respectively. A breakdown of the first type would be possible under moderate discharge conditions in helium and neon but not in argon, and would yield ionized nitrogen molecules. It is very probable that when these are excited the negative band spectrum † of nitrogen results, and this accounts for its appearance in helium and neon in contrast with argon. The second reaction leads to the formation of neutral nitrogen atoms, which may then be excited to give the arc lines of nitrogen. This breakdown would be possible only in helium, but under energetic conditions might be obtained to some degree in neon. It has been recorded in the present paper that during the development of the arc lines of nitrogen in neon the discharge-tube glowed with a brilliant yellow light, so that it is possible that some neon atoms were excited above the first ionization level. This may explain the partial development of the arc spectrum of nitrogen in neon. From the third reaction are liberated ionized nitrogen atoms which are capable of giving the spark lines, but this reaction could take place in helium only if conditions are energetic enough to pass the first ionization limit. Indeed, Merton and Pilley found that some spark lines appeared if intense discharges were used, but under moderate conditions they were absent. It is stated at the beginning of the discussion in accordance with Merton and Pilley's interpretation of experimental results, that the

* Proc. Roy. Soc. A. civ. p. 121 (1923).

† *Cf.* origin of negative carbon bands.

excitation potential of the N.I. spectrum probably lies in the neighbourhood of 11·8 volts, but as these results have been explained alternatively this statement cannot now be sustained. It must, of course lie below the ionization potential of helium.

According to the view put forward above, it would now appear that the inert gas used plays several parts in the production of spectra requiring the ionization or complete disruption of a molecule.

(1) It limits the energy available for breaking down the molecule.

(2) It conserves the products of disruption as explained by Merton and Pilley.

(3) It limits the energy available for exciting these products.

It is suggested that energy is imparted to the gas, which is present only in small quantities, not so much by direct electron impact as through the medium of the excited atoms of the inert gas.

It will be noticed that the presence of the inert gas permits of the production of such spectra as have been dealt with in two stages, and this may account for the ease with which they are developed by this method. Under the ordinary method of producing, say, the negative band spectrum of Nitrogen from low pressure Nitrogen, it seems inevitable that sufficient energy must be imparted by a *single* electron collision (*a*) to ionize the Nitrogen molecule ; (*b*) to excite this ionized molecule.

A similar explanation would appear to hold in the case of *uncondensed* discharges through high-pressure inert gas. For example, the comet-tail bands and associated bands and the negative carbon bands, all of which arise from a CO ion*, may be developed in two stages just as the negative nitrogen bands are produced. The inert gas again probably imposes a limit to the energy available for exciting spectra, but in the absence of experimental data it is difficult to assign the limit with certainty.

It is perhaps worthy of note that in the case of helium and neon at high pressure and excited by uncondensed discharges, the arc spectrum of the gas is developed, but in the case of argon under similar circumstances, few if any of the lines of the inert gas are produced, the arc spectrum being replaced by a blue continuous spectrum. What the

* Birge, 'Nature,' Aug. 1st, 1925, p. 170, and Aug. 8th, 1925, p. 207.

significance of this may be is not clear, but it would seem to suggest that the argon atoms possess very little energy which is capable of transference to molecules of other gases present. This may explain the inactivity of argon in the development of spectra which are produced well in neon and helium.

I wish in conclusion to express my sincere thanks to Dr. R. C. Johnson, under whose supervision the work was carried out.

XXXIII. *The Character of the Ionization produced by Spraying Water.* *By* P. J. Nolan, *M.Sc., Ph.D., University College, Dublin* *.

IN an examination of the electrification caused by spraying water, J. J. Nolan † came to the conclusion that the ionization produced consisted of a number of groups of ions having distinct mobilities. These groups were spread out over a very wide range, the mobility values extending from about the value attributed to ordinary "small" ions to that found for the Langevin or "large" ions. Similar groups of ions were discovered by J. A. McClelland and P. J. Nolan in the ionization produced by bubbling air through mercury. Further work gave corresponding results in the case of ionization produced in air bubbled through alcohol and also in air passed over phosphorus ‡. The alcohol and phosphorus ions corresponded very closely, the groups being about twice as numerous as in the case of the ions derived from spraying water. In the case of the larger ions the ratio between successive mobilities was about 3·4 for the water spray and 1·8 or $\sqrt{3{\cdot}4}$ for the other sources of ionization. There was fair agreement between the mobility values of the groups of ions produced in different ways, certain ions, for example those of mobilities ·00033, ·0012, and ·0041 cm./sec/volt/cm., being found in every case. In all these experiments the McClelland method of measuring mobilities was used.

The existence of these distinct groups of ions was called in question by Blackwood §. In his experiments the

* Communicated by Prof. J. J. Nolan, M.A., D.Sc.

† J. J. Nolan, Proc. Roy. Irish Acad. xxxiii. (A) p. 9 (1916).

‡ J. A. McClelland and P. J. Nolan, Proc. Roy. Irish Acad. xxxiii. (A) p. 24 (1916); xxxiv. (A) p. 51 (1918); xxxv. (A) p. 1 (1919).

§ Blackwood, Phys. Rev. xvi. p. 85 (1920).

ionization was produced by spraying water and by passing air over a hot platinum wire, and the nature of the ionization was examined by the Zeleny divided-electrode method. Blackwood held that his results showed that the sizes of the ions produced in these cases were spread out evenly over a wide range; in other words, he found "a continuous spectrum of mobilities and not a band spectrum." The present writer*, however, using the Zeleny divided-electrode method produced convincing evidence of the group character of the ionization due to alcohol and phosphorus and gave reasons for Blackwood's failure to obtain this result.

The question has been reopened by Busse †, who failed to detect ion-groups using both the single-electrode and the divided-electrode methods and producing the ionization by spraying water. He states that he has clearly proved that the ions produced by breaking up water cannot be classed in distinct groups but distribute themselves continuously and without gaps over a range the limits of which can be established by determining the largest and the smallest ions present. He is further of opinion that the step-like character of the ionization produced by other methods is extremely doubtful. The present writer considers that in the case of alcohol and phosphorus the evidence already produced for the group character of the ionization is unassailable. As the discontinuity of the ionization due to spraying water has only been shown by the single-electrode method in the earlier experiments, the work described in this paper was undertaken with a view to a further examination of the spray ions by the Zeleny method, which on account of its superior resolving power is specially suited to determine the points at issue.

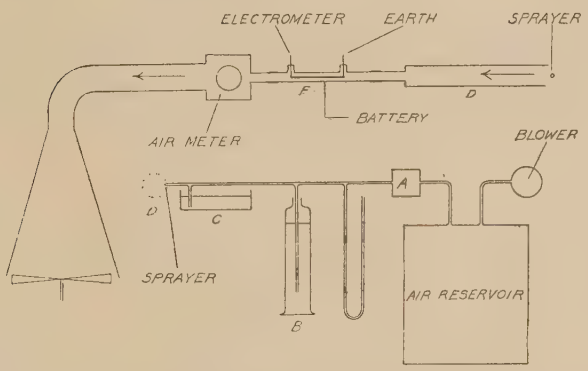
Experimental Method.

The experimental arrangements varied considerably in the course of the work. It was found that the character of the results depended a great deal on the type of sprayer used. Practically all the results which are quoted were obtained with the arrangement finally adopted which is now described. Fig. 1, the upper part of which is approximately to scale, gives a diagram of the apparatus. A rotary pump forced an air blast, the fluctuations of which were damped by a large air reservoir, through a cotton-wool plug A. The air thus purified, actuated a de Vilbiss sprayer which

* P. J. Nolan, Phys. Rev. xviii. p. 185 (1921).
† Busse, *Ann. der Phys.* lxxvi. p. 493 (1925).

drew distilled water from the vessel C. This vessel had a large cross-section, and as the consumption of water by the sprayer was small, the level of the water in C did not change appreciably during an experiment. The spraying pressure was kept constant by inserting a side tube which opened beneath the surface of mercury in the cylinder B. The pump was worked at such a rate that air bubbled continually through the mercury in B. This device for keeping the pressure constant was at a distance of about 150 cm. from the sprayer. Test experiments showed that ions due to air bubbling through the mercury could not be detected in the measuring apparatus. The sprayer was

Fig. 1.



placed with its nozzle close to the end of the tube D so that the spray was at right angles to the axis of the tube. A fan driven by a synchronous motor drew a constant air stream through the tubes D and F, the latter being the Zeleny condenser with divided electrode. The quantity of air passing per second was measured by means of an air-meter.

The dimensions of the Zeleny apparatus were as follows :—

Internal diameter of outer tube (b)	= 3	cm.
External diameter of electrode (a)	= ·95	cm.
Length of insulated electrode	= 5	cm.
„ „ earthed electrode	= 10	cm.
Total length of electrodes + gap (L)	= 15·2	cm.

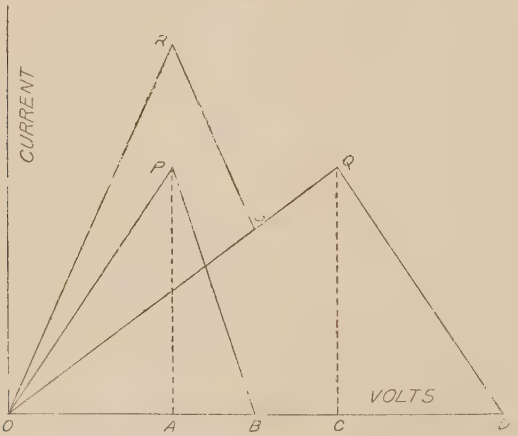
The volume of tube D and its connexion up to the end of electrode was 1450 c.c. The air-current in most of the experiments was 670 c.c. per sec. The insulated electrode was connected to a Dolezalek electrometer giving

2800 mm. scale divs. per volt. The connexion was protected in the usual way by an earthed guard-ring. A condenser, the capacity of which varied in different experiments from ·004 to ·007 m.f., was connected in parallel with the electrometer. The insulated and the earthed electrodes were connected by an ebonite plug which left a gap of 2 mm. between them. The outer tube was in metallic connexion with tube D and with the sprayer and could be raised to any desired voltage.

The Zeleny Double-Electrode Method.

As the question at issue in these investigations depends upon the evidence for the existence of separate and distinct groups of ions given by the Zeleny method, it may be of advantage to consider briefly the theory of the method. The ionized air is drawn through a tube with two central electrodes separated by a short gap. The electrode nearer the entrance to the tube is earthed and the other electrode

Fig. 2.



is insulated and connected to an electrometer. The currents to the insulated electrode for various voltages applied to the outer tube are observed and a curve is plotted with the voltages as abscissæ and the current values as ordinates. If only one type of ion is present in the air and if the ionization is originally uniform over the cross-section of the tube, a curve of the type OPB shown in fig. 2 should be obtained. This is drawn for the case when the insulated electrode is half the length of the earthed electrode. As

the voltage is increased from zero to value OA the current increases uniformly. Saturation occurs for voltage OA, and AP represents the maximum current to the shorter electrode which is one-third the total saturation current. On further increasing the voltage, the current decreases uniformly and for voltage OB or $\frac{3}{2}$ OA all the ions are captured on the earthed electrode. In practice, the curve OPB would be rounded off owing to diffusion of the ions, distortion of the electric field at the ends of the electrodes, etc. Curve OQD represents the curve due to an ion of one-half the mobility of the first ion and present in equal quantity, the saturation voltage OC being twice OA. To find the curve due to these two types of ions if present at the same time, the ordinates are added and curve ORSQD is obtained. Thus if two types of ions are present, a two-peaked curve should be found. Similar reasoning will apply to any number of classes of ions. A peak will represent a distinct type of ion, and the mobility of the ion can be calculated from the voltage corresponding to the peak from the formula

$$UV = \frac{Q \log_e \frac{b}{a}}{2\pi L},$$

where U = mobility,
V = critical voltage,
Q = volume of air passing per sec.

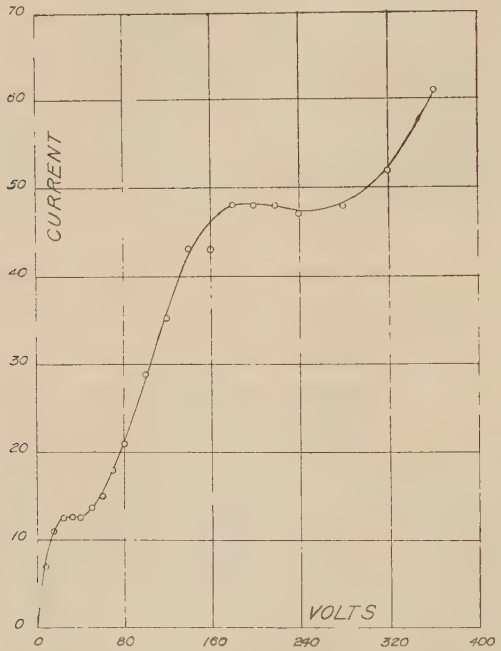
The character of the curve obtained in practice depends on the ratio of the lengths of the electrodes, on the ratio between successive mobilities, and on the number and relative quantities of the different classes present. The rounding-off of the curve for the various reasons cited may have the effect of obscuring some of the peaks. In curve ORSQD for example, observations may give the part of the curve SQ as a line parallel to the voltage axis, so that peak Q may not be well marked. A change in the mobilities of the ions as they pass along the tube will also tend to obscure the peaks, so that to get distinct evidence of separate groups, if they are present, it is necessary to reduce the time of the ions in the electric field as much as possible.

Results of Observations.

Fig. 3 gives the result of an examination of ions the age of which was over 2 secs. when they entered the electric field. The time spent in the field was ·14 sec. The current-

voltage curve refers to negative ions and was taken over the range 0–360 volts. It shows two discontinuities which represent peaks smoothed over in the fashions that have been suggested. The fact that the curve is rising at the higher voltages indicates that at least one other peak is present. When observations were further extended it was found, in fact, that the curve reached a maximum at about 650 volts and then descended. Now if the current-voltage relation is really of the kind shown in this curve, only one

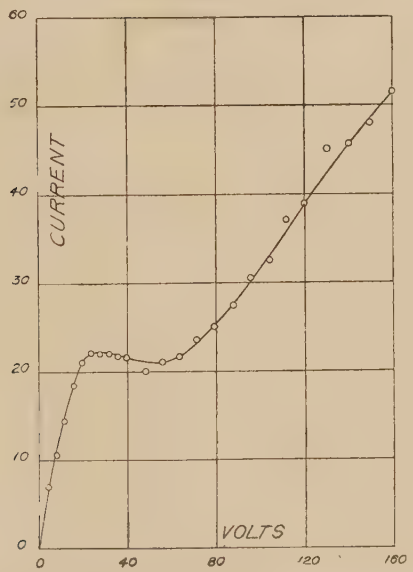
Fig. 3.



interpretation can be admitted, and that is that there are present at least three separate and distinct classes of ions. For if only one sharply defined class of ion is present, there should be one fairly sharp peak. On the other hand if, as Busse holds, the ions are of sizes which vary continuously over a fairly wide range, the curve should not only show a wide summit (the width being determined by the limits of the range) but should be smooth and convex throughout. The curve obtained is practically linear between the discontinuities and is a fair approximation to a portion of the

complete theoretical curve for a mixture of ions of different classes. It differs in shape from the curve given in fig. 2 because in that case only two kinds of ions were assumed to be present, and those in equal quantities. Here the first two classes which are disclosed are present in smaller quantities than the remaining group or groups, and the discontinuities appear in consequence on the left-hand side of the highest part of the curve. It is impossible that there could be any doubt as to the interpretation of a curve like that of fig. 3. The only question remaining, therefore, is whether the experimental evidence gives sufficient justification for drawing it as it has been drawn. This can be tested by working over the curve in closer detail.

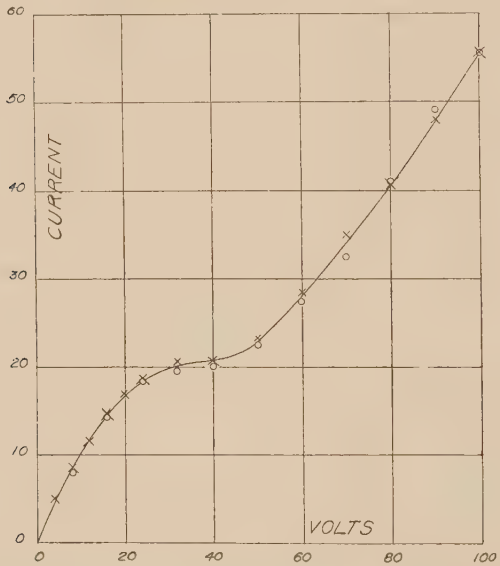
Fig. 4.



In fig. 4 is given the result of a close examination over the region 0–160 volts. This curve shows a peak at 28 volts corresponding to the first discontinuity in fig. 3. In general shape it corresponds very accurately with the theoretical Zeleny curve and discloses the existence of two distinct classes of ions. Thus the ascending parts are very nearly straight lines passing through the origin. In the earlier part of this paper the measures taken to secure steadiness were indicated. That they were successful is

shown by the accuracy with which observations could be repeated. Thus in fig. 5 two series of observations are plotted over the range 0–100 volts. One series was taken immediately after the other, and the close agreement between them shows how steady all the conditions were and disposes of the argument that fluctuations in the sprayer, in the air-current or in the field-voltage could account for the discontinuities. Moreover, it would be indeed strange if imperfections in the apparatus and irregularities in the method of working could occur in such a way as always to simulate a peak in the same part of the curve. It is not

Fig. 5.

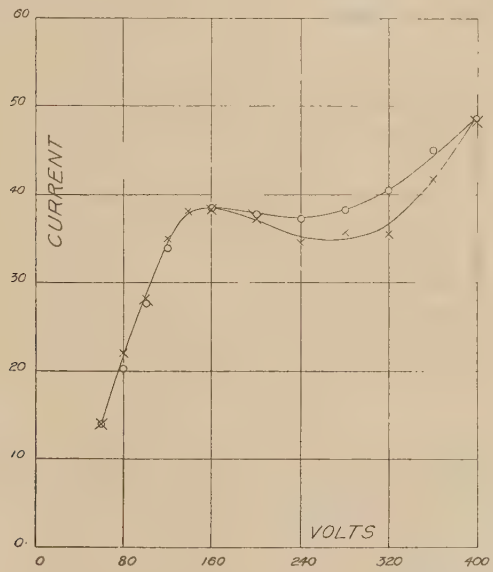


pretended that the apparatus used was perfectly adapted to secure the theoretical Zeleny curve. For example, small errors in the centreing of the electrode no doubt existed. It would also be impossible under the conditions of experiment to secure absolute uniformity of the ionization over the cross-section of the tube. But the singularities shown on the curves could not arise out of such causes.

There is a real variation from day to day which affects not the existence of a peak but its degree of prominence. Thus the first peak is much more marked in fig. 4 than in fig. 3 or fig. 5. The same sort of variation is shown

in fig. 6 which shows the results of observations made on two successive days over the range 60–400 volts corresponding to the higher peak on fig. 3. The numbers plotted are, with six exceptions, the means of readings taken with ascending and descending voltages. While the day's interval has altered the shape of the curve, it has not obliterated the peak or altered its position. The mean value found in various curves for the position of this peak was 170 volts.

Fig. 6.



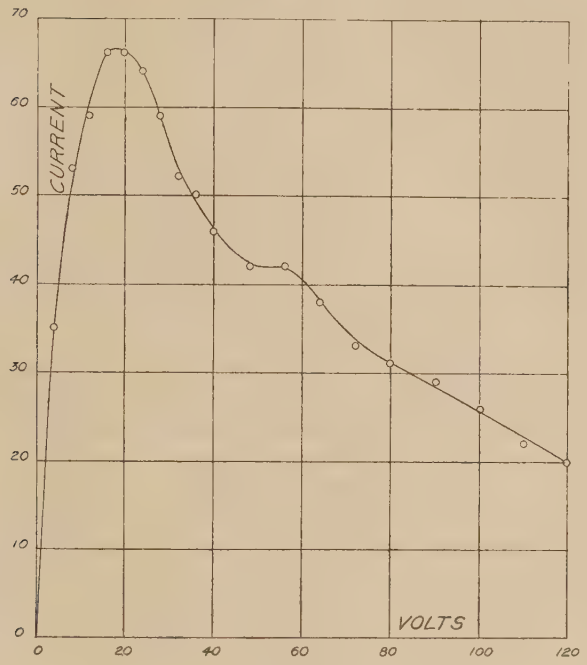
The curves obtained, of which those reproduced form a selection, enable us to fix with fair accuracy the positions of the two peaks at 30 volts and 170 volts. The next peak was found, as has been stated, at about 650 volts. The mobilities calculated from these critical voltages are ·27, ·047, and ·012 cm./sec./volt/cm. These ions apparently correspond to the ions of mobilities ·24, ·046, and ·013 observed by J. J. Nolan in his original examination of the ionization from a water-spray. He found also an ion of mobility ·12, which is not disclosed in the curves that have been examined. In the ionization produced by bubbling air through mercury, groups of ions of mobilities ·20 and ·048 appear without any intermediate

group. It is possible that in the present work the non-appearance of the ion of mobility ·12 is due to some change in the conditions of experiment, *e.g.* to the use of a different type of sprayer. If this ion had appeared in the present experiments, it would have caused a peak in the current-voltage curve at 67 volts and thus would have filled up the marked concavity in the curve. In fact it is to the non-appearance of such a peak that the curves reproduced owe their convincing character. The change in the forms of the peaks from day to day may be ascribed to the presence of this or other ions in small and varying quantities.

The results so far given support in the fullest fashion the conclusions previously advanced as to the character of the ionization and, as far as they go, are in numerical agreement with the previous results. Nothing more than this was contemplated in the present work, for to cover the whole ground once more and to work over all the types of ions previously found would involve a very extensive series of observations the necessity for which has not been shown.

Reference was made earlier in this paper to the fact that different results were obtained using different types of sprayer. The difference was not in the essential character of the ionization, but in the way in which the groups occurred. To illustrate this point an example is given in fig. 7 of a curve obtained with a sprayer differing from that used in the work already dealt with. This curve shows a well-marked peak at 18 volts and indications of a peak at 55 volts. The mobilities corresponding to the voltages are ·36 and ·12 (the air-current also differed in this case). The general shape of the curve so far as it has been plotted is due to the fact that the ion of mobility ·36 is present in considerable quantity. The ion of mobility ·27 which was so prominent in the previous cases does not appear here, whereas there are indications of the presence of the ion of mobility ·12 previously missing. The ion of mobility ·36 probably corresponds to that of mobility ·32 or ·31 found with mercury and alcohol. Possibly we have in this curve an explanation of Busse's failure to detect separate groups of ions. Under certain conditions of experiment the groups might occur in such relative quantities that the current-voltage curve resulting would with difficulty be distinguished from a smooth curve. For example, a long and careful working over the curve in fig. 7 would be necessary to prove conclusively the existence of a discontinuity at 55 volts.

Fig. 7.



Conclusions.

It has been shown that when water is sprayed, the ions produced assume preferentially certain definite sizes. Whether they are exclusively of these sizes or whether there is in addition a general background of ionization covering all sizes, our experiments are not critical enough to detect. But combining the present work with that previously reported, it is clear that by a variety of processes a series of groups of ions can be produced, the same ions tending to appear whatever the origin of the ionization. Some of the complexity of the ionization might be explained by assuming the existence of multiple charges on some of the ions, but a study of the mobility values will show that very little simplification can be achieved in this way. We must assume that the ions are of many different stable or semi-stable sizes. Reasons have been given for believing that the ions are composed of water *. The results then suggest that there must be a variety of water aggregates

* J. J. Nolan, Proc. Roy. Soc. A. xciv. p. 112 (1917).

each enjoying a certain degree of stability. J. J. Thomson * and Langevin † have shown theoretically the possibility of the existence of a water-spherule of a certain size which would be stable even in dry air. The existence of this complex ionization suggests that there must be several such stable sizes.

It may be remembered in this connexion that in addition to the "small" ions and the Langevin or "large" ions found in atmospheric air, Pollock ‡ has found an ion of mobility ·02 in dry air in Sydney. Dorno § found at Davos ions of mobility ·04, and Knoche ‖ over the Pacific ions of mobility ·05. While Pollock's ion does not fit readily into our scheme, the ions found by Dorno and Knoche may very well correspond with the ion of mobility ·047 which is disclosed in the present work and which was prominent in the previous experiments. It is possible even that the whole series of ions exist to some degree in atmospheric air. The problem presented by these ions is a problem in the physics of small aggregates of water. That they are charged is an accident due to their method of production, due for example in the spraying and bubbling of liquids to the fact that rupture of electrical double layers occurs. But the sizes of the ions tell us nothing about the constitution of these double layers, any more than the ions of identical sizes produced from phosphorus tell us anything about the manner of their production.

XXXIV. *Measurement of the Resistance of a Condenser at Radio Frequency.* By Charles D. Callis, *Assistant in Physics, Indiana University, U.S.A.* ¶

It appears that the resistance of a condenser has not been measured at radio frequencies. All measurement of the losses of a condenser at radio frequency has been made by comparative methods. It is customary to measure the resistance of a standard condenser at low frequency (one or two thousand cycles) and, if the resistance is low or negligible, to consider the resistance at high frequency to be zero. This is based on the fact that dielectric losses diminish

* 'Conduction of Electricity through Gases,' p. 149 (1903).
† See Chauveau, *Le Radium*, March–April, 1912.
‡ Pollock, *Le Radium*, p. 129 (1909). Phil. Mag. xxix. p. 636 (1915).
§ C. Dorno, *Licht und Luft im Hochgebirge*, Braunschweig, 1911.
‖ W. Knoche, *Phys. Zeitschrift*, xiii. p. 322 (1912).
¶ Communicated by Professor R. R. Ramsey.

with frequency *. The resistance of a given condenser is compared with a standard by placing the condenser in a high-frequency circuit and measuring the resistance of the circuit, and then replacing the condenser with the standard and measuring the resistance of the circuit again, the difference in the two results being due to the difference of resistance of the two condensers. Since the resistance of the standard is assumed to be zero, the difference is the resistance of the condenser.

The investigation, of which this article is a report, is the result of a method devised by Professor R. R. Ramsey, of Indiana University, and worked out under his direction by the writer. It is an attempt to make absolute measurements of the resistance of a variable condenser at a frequency of one million cycles per second.

The method of measuring radio frequency resistance of a circuit is very simple. A radio frequency galvanometer or milliammeter is placed in the circuit of a coil and a condenser. This circuit is tuned so as to be in exact resonance with an oscillating circuit and the current noted in the meter. A known resistance is inserted and the current noted again. From these readings the resistance of the circuit is determined. A particular case is the half-deflexion method, in which resistance is inserted until the current is reduced to half the original value and then the resistance of the circuit is equal to that of the resistance inserted. The resistance as measured is that of the coil, of the condenser, and of the meter. The meter is usually so constructed that its resistance is the same as the D.C. resistance. The problem is to separate the resistance of the condenser from that of the coil.

It is well known that the resistance of a straight wire is larger for alternating current than for direct current, due to the skin effect. It is also known that the high-frequency resistance of a wire is different when it is coiled from that when it is straight and far removed from other wires. The impedance of a coil at high frequency is so great that it is practically impossible to force an appreciable amount of current through the coil without placing it in connexion with a condenser and tuning the circuit. The measurement of the resistance of the coil without the condenser is out of the question.

The method used in this investigation is to wind two coils as nearly alike as possible. Coil No. 1 is placed in series

* Bureau of Standards, Bulletin 74, pp. 113, 126, 190. Louise McDowell, Phys. Rev. xxiii. p. 507 (1924).

with the condenser and meter and tuned to the same frequency as that of the generator, and the resistance of the circuit measured by the method described above. Coil No. 2 is then inserted, and since it is nearly the same as No. 1 the setting of the variable condenser is approximately the same as in the first case. The resistance of this circuit is then measured.

Adding the two results gives the equation:

$$R_1 + R_2 = r_1 + r_2 + 2C + 2m. \quad . \quad . \quad . \quad . \quad (1)$$

R_1 and R_2 are the two measured resistances, r_1 and r_2 are the resistances of the coils, C the resistance of the condenser, and m is the resistance of the milliammeter. The two coils are then placed in series opposition in the circuit with the condenser and milliammeter, and their positions adjusted so that the combined inductance of the two is equal to the inductance of one coil. The circuit is then in resonance with the generator with the condenser set at the same capacity. Then the resistance R_3 of the circuit is measured.

$$R_3 = r_1 + r_2 + C + m. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Subtract equation (2) from equation (1) we get

$$(R_1 + R_2) - R_3 = C + m. \quad . \quad . \quad . \quad . \quad (3)$$

Since m is known, the value of the resistance of the condenser at a particular setting has been determined. This is true provided the resistances of the two coils placed in series opposition is the sum of the separate values. From the above readings it is possible to determine the resistances of the coils as well as the resistance of the condenser. Preliminary measurements were made with coils of No. 20 copper wire. These measurements suggested making the coils of fine wire. Coils were then constructed of No. 36 copper wire, the A.C. resistance of which, according to tables already compiled, is not more than ·6 per cent. greater for one thousand kilocycles than for direct current. Checking through with coils made of this wire and solving for the resistance of the coils we get a result which, within the accuracy of the apparatus, is the same as the D.C. resistance of the coils. Therefore the assumption is made that changing the relative position of coils made of No. 36 or No. 40 wire does not change the resistance of the coils, and the value obtained for the condenser is the true resistance of the condenser. Nine pairs of coils were made with this fine wire. The number of turns was adjusted to give readings at various points on the condenser scale.

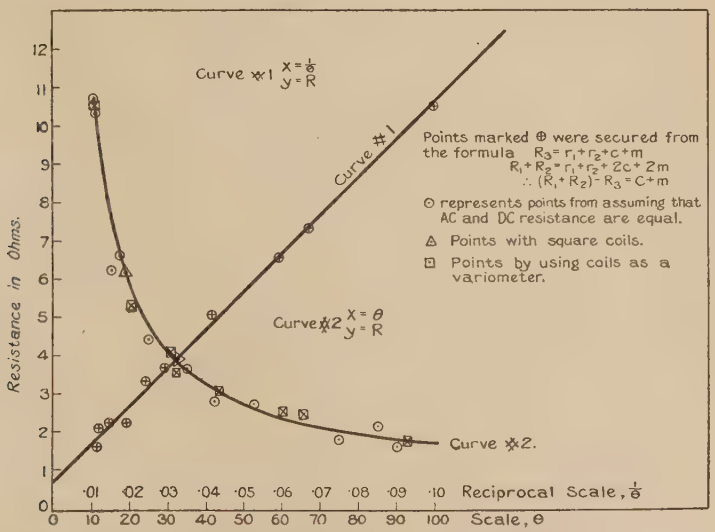
The condenser used was a commercial forty-one plate

variable air-condenser with semicircular plates of the "low loss" type. In this condenser the capacity is directly proportional to the dial readings, the maximum capacity being 0·001 microfarad. The resistance of the condenser was found to vary inversely with the capacity.

The resistance as found with the nine sets of coils and the reciprocal of the dial readings are plotted in the figure giving the straight line, Curve No. 1. Curve No. 2, which is an equilateral hyperbola, is plotted from data taken from the straight line. The equation of the straight line is

$$R = 0{\cdot}75 + \frac{99}{\theta},$$

where θ is the scale-reading at any particular setting.


Curve #1 X = 1/θ Y = R
Curve #1
Points marked ⊕ were secured from the formula R3 = r1 + r2 + c + m
R1 + R2 = r1 + r2 + 2c + 2m
∴ (R1 + R2) − R3 = c + m
⊙ represents points from assuming that AC and DC resistance are equal.
△ Points with square coils.
⊡ Points by using coils as a variometer.
Curve #2 X = θ Y = R
Curve #2.
Resistance in Ohms.
Reciprocal Scale, 1/θ
Scale, θ
0 1 2 3 4 5 6 7 8 9 10 11 12
·01 ·02 ·03 ·04 ·05 ·06 ·07 ·08 ·09 ·10
0 10 20 30 40 50 60 70 80 90 100

Since the calculated value of the resistance of the coils was approximately the same as that of the D.C. resistance, other measurements were made with single coils of No. 36 wire, the resistance of which was assumed to be the measured D.C. resistance. The values of the resistance of the condenser are shown on the curve by the circled points. Coils made of No. 40 wire were used in the same manner, and the values of the resistances indicated in the same way. Measurements were also made with two coils in series, and their relative positions changed so as to change the inductance and thus get several settings of the condenser. The values of these resistances are indicated on Curve No. 2 by crossed squares.

The coils were made in the Lorentz form in which the wire is interwoven on pegs set in a circle, tied with cotton cord, and then removed from the forms. The coils were then self-supporting without a core. Since all the coils have been wound after the same pattern, it was thought that there might be danger of a systematic error due to the form of the coil. Coils were wound on wooden cross-arms, making square coils about 50 centimetres on a side. The turns in these coils were placed 1 centimetre apart. Measurements of the resistance of the condenser using these coils are shown on Curve 2 by points in triangles.

It will be noted that all these points follow the equilateral hyperbola, showing that all results are the measurement of the resistance of the condenser, and not some change in resistance of the coils due to placing wire in the field caused by a current in other wires.

The points do not lie on the curve exactly. This is due to the fact that the absolute error made in measuring the total resistance of the circuit appears with the value of the condenser resistance. The total resistance of the circuits varied from 10 ohms for large capacity to 75 ohms for small capacity.

The oscillator was a 5-watt tube, with a 350 volt D.C. generator for plate supply. This generator was run by a motor on the regular University circuit. Any variation on the line caused a variation of the plate voltage and a variation of the output of the tube. These variations introduced large errors in the measurements. It is hoped to procure a more powerful oscillator and a constant potential plate supply and make more refined measurements of the resistance of a condenser.

The purpose of this article is to give a method by which the resistance of a variable air-condenser can be measured. The resistance is a measurable quantity, and the resistance of a "low loss" condenser is not small or zero as has been assumed by those who base their assumptions on dielectric measurements. This particular condenser has a resistance which varies from about 1·7 ohms to 15 ohms. If this high value is not true the only other assumption that can be made is, that given any number of coils made of the same size wire (No. 40) wound in any form whatever; various diameters, number of turns, and spacings; but wound so as to have the same inductance, then the difference between the A.C. resistance and the D.C. resistance is the same constant value for each coil.

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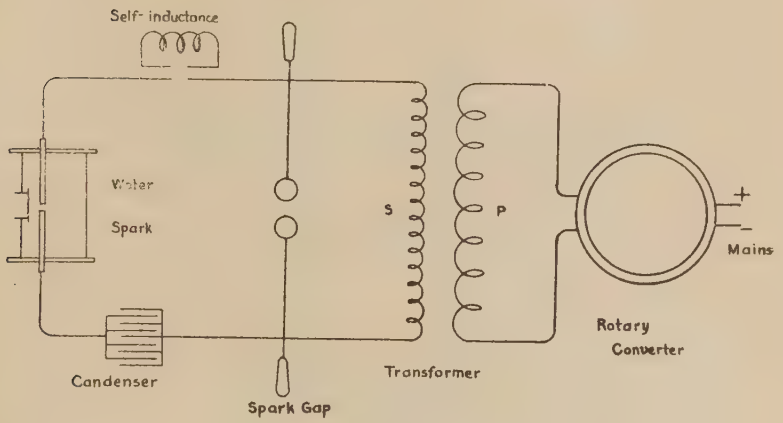
XXXV. *On the Water-Spark Absorption Spectrum of Iron.* *By* N. K. Sur, *M.Sc.* (*Physics Department, Allahabad University*) *.

[Plate VII.]

IT has long been known that when a spark is produced between two metal electrodes immersed in distilled water, it emits a fairly continuous light which is under certain conditions traversed by absorption lines of the metal of the electrode. The spectrum of the spark under water has been studied by Wilsing, Hale, Konen †, and in recent years by Victor Henri ‡ and his students, Hulburt §, and Angerer and Joos ‖.

The present investigation arose out of an attempt to see whether the water-spark spectrum can be used as a source

Fig. 1.



ARRANGEMENT FOR WATER SPARK.

of continuous ultra-violet light in place of other sources, *e.g.* the positive crater of the arc, or a tungsten lamp with quartz windows. As a result of these studies many new facts have been brought to light, and it has been found that

* Communicated by Professor M. N. Saha.

† Konen, *Ann. der Physik*, vol. ix. p. 779 (1902).

‡ Victor Henri, Proc. Roy. Soc. London, A, vol. cv. pp. 668-69 (1924)

§ Hulburt, Phys. Review, vol. xxiv. pp. 129-33 (1924).

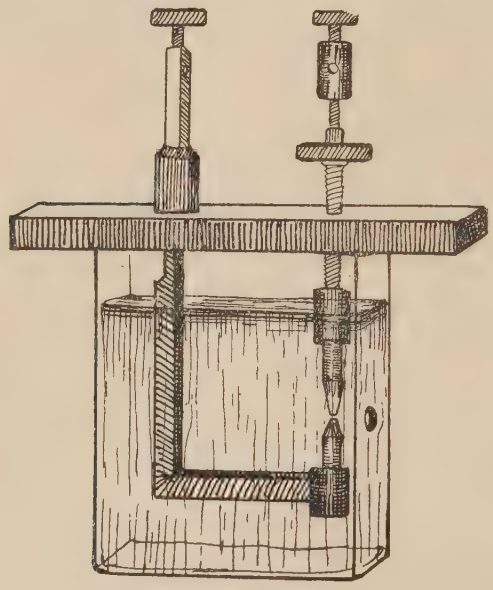
‖ Angerer & Joos, *Ann. der Physik*, vol. lxxiv. pp. 746-47 (1924).

the arrangement is very suitable for studying the absorption spectra of elements.

The apparatus employed is shown in figs. 1 and 1 *a*.

Transformer.—As shown in the diagram, the spark is produced under water by a high-frequency discharge from a high-tension transformer. T is a high-tension transformer of $\frac{1}{4}$ KW capacity. The primary of the transformer is furnished with alternating current from a rotary converter working at 110 volt D. C. The secondary furnishes an alternating e.m.f. of 15,000–20,000 volts, and works very smoothly.

Fig. 1 *a*.



Sparking vessel

Condenser.—As the leyden-jars are frequently punctured, we constructed a condenser after Millikan's pattern. This consisted of thick ($\frac{1}{2}$ cm.) window glasses 34×23 cm. with alternate sheets of zinc. The whole was placed under oil, in a porcelain tank. The advantage is that the capacity can be varied with the least amount of trouble within very wide limits, and if any plate is punctured, it can be immediately replaced.

It may be mentioned here that the potential to which the condensers can be charged depends on the rate of power-supply, as was first pointed out by Anderson *. It is no use trying condensers of large capacity unless the rate of power-supply is proportionately larger. When the given source of high tension has a definite rate of power-supply, there is a certain definite value of the capacity with which the apparatus works best.

The Sparking Vessel.—In the experiments of Victor Henri and Angerer and Joos a teak-wood vessel was used. This type of vessel was first tried, but as the sides were cemented by shellac and other adhesives, they leaked very badly. It was found that an ordinary glass cell was quite good for the purpose. A hole was drilled on one side which was stopped by means of a quartz window. The sparking pieces were carried by an ebonite lid, and were provided with sockets, into which rods of any metal could be inserted and fixed with a screw. The distance between the metallic pieces could be adjusted by screw-heads fixed to the ebonite lid. After sparking for some time the water gets dirty and cuts off the ultra-violet light. The water could be siphoned off through a hole at the top and fresh distilled water put in.

Working of the Apparatus.—It will be seen from the diagram that the discharge takes place in a high-frequency oscillatory circuit completed through the condenser, the water-spark, and the parallel spark-gap. The frequency of oscillation could be varied by inserting different self-inductances in the circuit. The nature of the spectrum emitted can, by this means, be varied within wide limits, as was found by Stücklen †. This point is the subject of a separate investigation by Mr. P. K. Kichlu, and will be published later. It has been found that if more self-inductances are inserted, the discharge emits, instead of a strong continuous spectrum crossed with absorption lines, a less continuous spectrum with superposed emission lines. In the present experiments the self-induction was cut down to the minimum value.

Mr. Kichlu has found that the geometrical form of the rods has a marked influence on the nature of the spectrum. Sharp-pointed electrodes always give emission lines. Flat electrodes gave a strong continuous spectrum with absorption lines. The spark was generally 3 to 4 mm. in length and 2 to 3 mm. in breadth, and emitted an intense bluish-white light.

* Anderson, Astrophys. Journal, vol. lix. pp. 76–96 (1923).

† Stücklen, *Zeits. für Physik*, vol. xxx. pp. 24–39 (1924).

Theory of the Water-Spark.

Victor Henri* has formulated a theory of the water-spark. According to him the aureole of light consists of an inner core composed of highly-ionized metallic vapour, surrounded by a cooler mantle of vapour. The inner vapour space emits a continuous spectrum, and the absorption lines are produced in the outer mantle of cooler vapour when it is traversed by the continuous light.

Besides the metallic lines, prominent absorption lines are obtained on all plates at about $\lambda = 3100$ A.U. They have been ascribed to $(O\bar{H})$ ions.

That very high pressure is developed inside the spark is at once apparent. After the spark has passed for some time, the electrodes appear as if their heads have been battered by a hammer. If the lower screw is not tight enough, the electrode is pressed downwards. The water in the vessel is in a violent state of agitation, and sometimes the quartz window breaks under pressure. It is possible to measure the pressure developed, but this has not been attempted as yet.

According to the theories of Eddington† and Saha‡, a typical star consists of a core of highly-ionized gas with an outer layer of cooler vapour containing neutral as well as ionized atoms. The water-spark is thus a miniature star, and if water could be replaced by some transparent compressed gas, like H_2 or He, probably the continuous spectrum could be extended by a substantial amount to the ultra-violet. With the present arrangement we have obtained the spectrum down to $\lambda = 2100$ Å.U. on Seed 40 plates. The times of exposure varied from 1 to 5 minutes in the region $\lambda = 3000$ Å.U.

This arrangement is considered to be a substantial improvement on that of Victor Henri and his co-workers, because they had to expose their plates from 3 to 45 minutes, while we have found generally 1 minute to be quite sufficient. We used a 5-foot concave grating with a ruled surface of $1\frac{1}{2}$ inches and giving a dispersion of 11·11 Å.U. per mm. in the first-order spectrum. Victor Henri used a quartz spectrograph which has more light-gathering power than our grating. I am now engaged in making a systematic study of the absorption spectra of elements with this

* Victor Henri, *vide* Stücklen's paper cited above.

† Eddington, Month. Not. Roy. Astro. Soc. vol. lxxxiii. p. 32 (1923); and *Zeits. für Physik*, vol. vii. p. 351 (1921).

‡ Saha, "On a Physical Theory of Stellar Spectra," Proc. Roy. Soc. A, vol. ci. pp. 138–153 (1921).

apparatus. The first element studied was iron, and the results are reported below. A portion of the iron spectrum at about $\lambda=4000$ Å.U. photographed in the third-order spectrum is reproduced (see Pl. VII.).

Absorption Spectrum of Iron.

The lines which have been obtained in the water-spark as absorption lines are given in Table I. The wave-lengths are taken from the measurements of Burns *, rounded off to two places of decimals ; intensity and temperature class from King † ; and series classification from the recent work of Laporte ‡. Many weak lines, which are not to be found in Laporte's list, have been obtained in absorption.

TABLE I.

Iron lines obtained in water-spark as absorption lines.

Wave-lengths (Burns).	Wave-numbers (vacuum).	Intensity & temperature class (King).	Series notation (Laporte).	Remarks.
4071·75	24552·57	40 II	$\overline{F}^1_2 - F^1_2$	
4063·60	24601·78	45 II	$\overline{F}^1_3 - F^1_3$	
4045·82	24709·91	60*r* II	$\overline{F}^1_4 - F^1_4$	
3930·30	25436·14	25R I	$d^1_2 - \overline{d}^1_3$	
3927·93	25451·45	30R I	$d^1_1 - \overline{d}^1_2$	
3922·92	25484·03	25R I	$d^1_3 - \overline{d}^1_4$	
3920·26	25501·31	20*r* I	$d^1_0 - \overline{d}^1_1$	
3902·95	25614·41	20 II	$\overline{F}^1_3 - \overline{D}^1_3$	
3899·71	25635·67	30R I	$d^1_2 - \overline{d}^1_2$	
3898·01	25646·86	10 II	$\overline{f}^1_1 - \overline{d}^2_2$	
3895·66	25662·35	25*r*	$d^1_1 - \overline{d}^1_0$	
3887·05	25719·16	15 I	$\overline{f}^1_4 - \overline{d}^2_4$	
3886·29	25724·24	40R I	$d^1_3 - \overline{d}^1_3$	
3878·58	25775·35	100R II	$d^1_2 - \overline{d}^1_1$	
3878·02	25779·05	60R II	$\overline{f}^1_3 - \overline{d}^2_3$	
3872·51	25815·77	60R II	$\overline{f}^1_2 - \overline{d}^2_2$	

* Burns, *vide* Kayser-Konen, *Handbuch der Spectroskopie*, vol. vii.

† King, Astrophys. Journ. vol. xxxvii. p. 239 (1913), and vol. lv. p. 318 (1922).

‡ Laporte, *Zeits. für Physik*, vol. xxiii. p. 135 (1924), and vol. xxvi. p. 1 (1924).

TABLE I. (*continued*).

Wave-lengths (Burns).	Wave-numbers (vacuum).	Intensity & temperature class (King).	Series notation (Laporte).	Remarks.
3865·53	25862·38	40*r* II	$\bar{f}_1^1 - \bar{\bar{d}}_1^2$	
3859·91	25900·00	300R I	$d_4^1 - \bar{d}_4^1$	
3856·37	25923·77	100R IA	$d_3^1 - \bar{d}_2^1$	
3850·82	25961·16	15*r* II	$\bar{f}_2^1 - \bar{\mathrm{P}}_2^1$	Breaks the selection-principle.
3841·05	26027·17	80*r* II	$\bar{\mathrm{F}}_2^1 - \bar{\mathrm{D}}_1^1$	
3834·23	26073·50	80R II	$\bar{f}_3^1 - \bar{d}_2^2$	
3827·83	26117·10	75*r* II	$\bar{\mathrm{F}}_3^1 - \bar{\mathrm{D}}_2^1$	
3825·89	26130·35	125R II	$\bar{f}_4^1 - \bar{d}_3^2$	
3824·44	26140·19	100R IA	$d_4^1 - \bar{d}_3^1$	
3820·43	26167·66	200R II	$\bar{f}_5^1 - \bar{d}_4^2$	
3815·84	26199·11	100*r* II	$\bar{\mathrm{F}}_4^1 - \bar{\mathrm{D}}_3^1$	
3767·19	26537·43	60R II	$f_1^1 - f_1^2$	
3763·59	26561·42	80R II	$\bar{f}_2^1 - f_2^2$	
3758·23	26600·71	125R II	$\bar{f}_3^1 - f_3^2$	
3749·49	26662·76	125R II	$\bar{f}_4^1 - f_4^2$	
3748·26	26671·45	125R IA	$d_1^1 - f_2^1$	
3745·90	26688·31	80R IA	$d_0^1 - {}^1f_1$	Not clearly resolved.
3745·56	26690·69	150R I	$d_2^1 - {}^1f_3$	
3743·36	26706·35	40R IIA	$\bar{f}_2^1 - {}^2$	
3737·14	26750·88	200R I	$d_3^1 - {}^1f_4$	
3734·87	26767·12	150R II	$\bar{f}_5^1 - f_5^2$	
3733·32	26778·22	80R IA	$d_1^1 - {}^1f_1$	
3727·62	26819·15	40R II	$\bar{f}_3^1 - {}^2f_2$	
3722·57	26855·57	100R I	$d_2^1 - {}^1f_2$	
3719·94	26874·53	300R I	$d_4^1 - {}^1f_5$	
3709·25	26952·00	40R II	$f_4^1 - f_3^2$	
3606·68	27718·45	20 III		
3586·99	27879·61	30 II	$f_2^1 - \bar{g}_2^1$	
3583·32	27899·14	2 IV		
3581·20	27915·62	250R I	$\bar{f}_5^1 - \bar{g}_5^1$	
3573·84	27973·15	4 IV		
3573·40	27976·59	2 IV		
3570·24	28001·36	20 III	.....	Not resolved.
3570·10	28002·43	100R I	$f_4^1 - \mathrm{G}$	

TABLE I. (*continued*).

Wave-lengths (Burns).	Wave-numbers (vacuum).	Intensity & temperature class (King).	Series notation (Laporte).	Remarks.
3565·38	28039·50	60*r* II	$\bar{f}_3^1 - \bar{G}_4^1$	
3560·71	28076·30	5 IV		
3547·20	28183·22	? ?		
3500·57	28558·63	2 IV		
3497·84	28580·9	40 I	$d_1^1 - p_2^1$	
3490·58	28640·3	100*r* I	$d_3^1 - p_3^1$	
3476·71	28754·6	40 I	$d_0^1 - p_1^1$	
3475·45	28765·1	70*r* I	$d_2^1 - p_2^1$	
3465·86	28844·6	60*r* I	$d_1^1 - p_1^1$	
3443·88	29028·8	50*r* I	$d_2^1 - p_1^1$	
3440·99	29053·2	75R I	$d_3^1 - p_2^1$	Not clearly resolved.
3440·61	29056·3	150R I	$d_4^1 - p_3^1$	
3427·13	29170·60	20 III	.....	Not resolved.
3426·99	29171·76	2 IIIA	$f^1{}_2 - p_2^2$	Breaks the selection-principle.
3407·47	29338·91	20 III		
3401·52	29390 18	6 III	$f_4^1 - p_3^2$	Breaks the selection-principle.
3399·34	29409·06	15 III		
3222·07	31027 03	20 III		
3182·99	31407·95	3 IV		
3119·50	32047·16	6 IV		
3100·67	32241·78	20 II	$\bar{f}_3^1 - \bar{d}_3^3$	Not clearly resolved.
3100·31	32245·56	20 II	$\bar{f}_2^1 - \bar{d}_2^3$	
3099·97	32249·05	15 II	$\bar{f}_4^1 - \bar{d}_4^3$	Not resolved.
3099·90	32249·79	20 II	$\bar{f}_1^1 - \bar{d}_1^3$	
3083·75	32418·71	20 II	$\bar{f}_2^1 - \bar{d}_1^3$	
3075·73	32503·25	25*r* II	$\bar{f}_3^1 - \bar{d}_2^3$	
3067·25	32593·04	30*r* II	$\bar{f}_4^1 - \bar{d}_3^3$	
3059·09	32679 98	100R I	$d_3^1 - \bar{d}_4^2$	
3057·45	32697·50	40R II	$f_5^1 - \bar{d}_4^3$	
3047·61	32803·10	100R I	$d_2^1 - \bar{d}_3^2$	
3037·39	32913·43	80R I	$d_1^1 - \bar{d}_2^2$	
3025·85	33039·01	50R I	$d_0^1 - \bar{d}_1^2$	
3024·04	33058·78	15*r* IA	$d_1^1 - \mathrm{P}_2^1$	
3021·08	33091·17	150R I	$d_3^1 - \bar{d}_3^2$	Not resolved ; comes as a broad line.
3020·64	33095·93	200R I	$d_4^1 - \bar{d}_4^2$	
3020·50	33097·53	100R II	$d_2^1 - \bar{d}_3^2$	

TABLE I. (*continued*).

Wave-lengths (Burns).	Wave-number (vacuum).	Intensity & temperature class (King).	Series notation (Laporte).	Remarks.
3017·63	33128·96	15*r* IA	$d_1^1 - \bar{d}_1^2$	
3008·14	33233·45	60R I	$d_1^1 - \bar{d}_0^2$	
3000·95	33313·08	100R I	$d_2^1 - \bar{d}_1^2$	
2999·52	33329·02	30R II	$\bar{f}_5^1 - f_5^3$	
2994·50	33384·84	100R ? I	$d_0^1 - \mathrm{P}_1^1$	Not sure.
2994·43	33385·54	100R I	$d_3^1 - d_2^2$	
2983·57	33507·13	125R I	$d_4^1 - \bar{d}_3^2$	
2981·45	33531·00	20*r* I	$d_3^1 - \mathrm{P}_2^1$	
2973·14	33624·72	60R I	$d_2^1 - f_3^2$	Not resolved; comes as a broad line
2973·24	33623·60	60R I	$d_3^1 - f_4^2$	
2970·11	33659·02	40R I	$d_1^1 - f_2^2$	
2966·90	33695·37	125R II	$d_4^1 - f_5^2$	
2965·26	33714·06	20 II	$d_0^1 - f_1^2$	
2957·37	33803·97	30R II	$d_1^1 - f_1^2$	
2953·94	33843·18	50R II	$d_2^1 - f_2^2$	
2950·25	33885·55	20*r* IV		
2947·88	33912·84	60R I	$d_3^1 - f_3^2$	
2936·90	34039·53	60R I	$d_4^1 - f_4^2$	
2929·01	34131·31	25*r* I	$d_3^1 - f_2^2$	
2912·16	34328·72	20*r* I	$d_4^1 - f_3^2$	
2874·18	34782·36	10	$d_4^1 - f_5^1$	Break the selection-principle analogous to the absorption of $1\,S - md$ lines of alkalies as shown by Datta, Proc. Roy. Soc. Lond. A, ci. p. 545 (1922).
2869·31	34841·38	10 I	$d_3^1 - \bar{g}_4^1$	
2851·80	35055·30	15*r* II	$\bar{f}_1^1 - \bar{g}_2^2$	
2843·97	35151·81	20*r* II	$\bar{f}_2^1 - \bar{g}_3^2$	? (Laporte).
2838·12	35224·26	10 III	$\bar{f}_2^1 - \bar{g}_2^2$	
2832·43	35295·02	25*r* II	$\bar{f}_3^1 - \bar{g}_4^2$	
2828·81	35340·18	7 III		
2825·69	35379·19	6 II	$d_4^1 - \bar{\mathrm{G}}_5^1$	Breaks the selection-principle.
2823·28	35409·40	20 II	$\bar{f}_3^1 - \bar{g}_3^2$	? (Laporte).
2813·29	35535·13	30R II	$f_4^1 - \bar{g}_5^2$	
2807·24	35611·72	2 III	$d_4^1 - \bar{g}_3^1$	Breaks the selection-principle.

TABLE I. (*continued*).

Wave-lengths (Burns).	Wave-numbers (vacuum).	Intensity & temperature class (King).	Series notation (Laporte).	Remarks.
2806·99	35614·88	20 II	.....	Doubtful.
2804·52	35646·25	20 II	$\bar{f}_4^1 - \bar{z}_4^{\ }$	? (Laporte).
2797·78	35731·34	15 III		
2795·55	35760·62	.....	$\bar{f}_4^1 - \bar{g}_3^2$	? (Laporte).
2795·01	35767·53	3 III	$d_4^1 - \bar{G}_4^1$	Breaks the selection-principle.
2788·11	35856·04	30 II	.....	Not resolved.
2787·94	35858·02	5 II	.....	
2778·23	35983·55	20 III	$\bar{f}_5^1 - \bar{g}_5^2$	? (Laporte).
2778·08	35985·49	3 III		
2772·08	36063·37	20 II	$d_2^1 - p_3^2$	Laporte gives the neighbouring line 2772·11 (int. 1) as $d_2^1 - p_3^2$, but this is evidently wrong.
2763·11	36180·44	4 III		
2761·79	36197·73	18 III		
2756·33	36269·38	20 I	$d_1^1 - p_2^2$	Not resolved.
2756·27	36270·23	3 ?	$d_3^1 - F_4^1$	
2753·69	36304·20	3 III		
2750·15	36351·00	25*r* II	$d_3^1 - p_3^2$	
2746·99	36392·74	20 III		
2744·53	36425·36	8 III	.....	Not clearly resolved.
2744·07	36431·44	10 II	$d_0^1 - p_1^2$	
2742·41	36453·53	30*r* II	$d_2^1 - p_2^2$	
2739·55	36491·56	? ?		
2737·31	36521·39	20*r* II	$d_1^1 - p_1^2$	
2735·48	36545·86	8 III		
2733·58	36571·26	15 II		
2730·98	36606·08	2 III		
2728·97	36633·03	2 ?	$d_1^1 - F_2^1$	Not resolved.
2728·83	36634·92	2 III	.....	
2728·03	36645·66	3 III	.....	
2723·58	36705·50	15 II	$d_2^1 - p_1^2$	
2720·91	36741·55	40*r* II	$d_3^1 - p_2^2$	
2719·04	36766·84	60R II	$d_4^1 - p_3^2$	

TABLE I. (*continued*).

Wave-lengths (Burns).	Wave-numbers (vacuum).	Intensity & temperature class (King).	Series notation (Laporte).	Remarks.
2717·79	36783·72	2 III		
2711·66	36866·87	4 III		
2704·00	36971·30	? ?		
2690·07	37162·66	2 III	$d_4^1 - F_3^1$	
2689·84	37165·92	2 III	.....	Not resolved.
2684·86	37234·85	? ?	.....	
2684·76	37236·23	? ?	.....	
2681·59	37279·63	? ?		
2669·50	37448·76	2 IV		
2651·72	37700·17	2 III		
2647·57	37759·26	3 III	$d_3^1 - D_3^1$	
2641·65	37843·86	4 III		
2635·82	37927·57	8 III		
2632·60	37973·89	2 IIIA	$d_2^1 - \bar{D}_2^1$	
2629·60	38017·28	2 III	$d_0^1 - \bar{D}_1^1$	
2628·30	38036·08	? ?		
2623·54	38105·08	5 III		
2623·38	38107·43	2 III	$d_1^1 - \bar{D}_1^1$	
2618·72	38175·22	2 III	$d_4^1 - \bar{D}_3^1$	
2618·03	38185·27	5 III		
2615·43	38223·23	? ?		
2613·84	38246·48	? ?		
2611·89	38275·04	? ?		
2606·84	38349·17	6 III		
2599·58	38456·27	6 III	.....	Not resolved.
2599·41	38458·79	? ?	.....	
2598·38	38474·03	? ?		
2593·53	38545·97	? ?		
2588·01	38628·19	8 III		
2585·89	38659·86	20 IV		
2584·54	38680·04	8 III		
2577·93	38779·21	?		
2576·70	38797·72	4 III		
2575·76	38811·87	? ?		
2574·37	38832·83	? ?		

TABLE I. (*continued*).

Wave-engths (Burns).	Wave-number (vacuum).	Intensity & temperature class King).	Series-notation (Laporte).	Remarks.
2570·86	38885·85	? ?	.....	Not resolved.
2570·54	38890·68	? ?	.....	
2566·92	38945·52	? ?		
2563·49	38997·64	? ?		
2562·54	39012·09	? ?		
2549·62	39209·92	10*r* III	$d_3^1 - d_4^3$	
2545·98	39265·71	10*r* III	$d_2^1 - \bar{d}_3^3$	
2540·98	39343·20	10R III	$d_1^1 - \bar{d}_2^3$	
2535·61	39426·34	8*r* III	$d_0^1 - d_1^3$	
2527·44	39553·82	15*r* II	$d_3^1 - \bar{d}_3^3$	
2522·86	39625·63	40R II	$d_4^1 - \bar{d}_4^3$	
2518·11	39700·36	12*r* II	$d_2^1 - \bar{d}_1^3$	
2512·37	39791·08	5*r* III	$d_3^1 - \bar{d}_1^3$	
2510·84	39815·25	15R II	$d_3^1 - \bar{d}_2^3$	
2501·14	39969·72	20R II	$d_4^1 - \bar{d}_3^3$	
2491·16	40129·79	20R II	$d_1^1 - f_2^3$	Not clearly resolved.
2490·66	40137·91	30R II	$d_2^1 - f_3^3$	
2489·76	40152·42	15*r* II	$d_0^1 - f_1^3$	
2488·15	40178·41	40R II	$d_3^1 - f_4^3$	
2484·18	40242·45	15R II	$d_1^1 - f_1^3$	
2483·54	40252·95	10 II	.....	
2483·28	40257·21	60R II	$d_4^1 - f_5^3$	Not resolved.
2479·78	40313·95	20R II	$d_2^1 - f_2^3$	
2479·48	40318·86	6 III	.....	
2472·91	40425·96	12R II	$d_3^1 - f_3^3$	
2472·88	40426·53	? ?	$d_2^1 - f_1^3$	Doubtful.
2465·16	40553·04	6 III		
2462·65	40594·35	10*r* II	$d_4^1 - f_4^3$	
2462·19	40601·94	4 III	$d_3^1 - f_2^3$	Doubtful.
2453·48	40746·10	5 III		
2447·72	40842·01	4 II?	$d_4^1 - f_3^3$	
2438·19	41001·59	2 III		

The group $d^1 - f^3$ (multiplet 8) has been obtained in absorption by Gieseler and Grotrian (*Zeits. für Physik*, vol. xxv. p. 342, 1924) in the furnace at a temperature of 1500° C.

Discussion of the Results.

The lines of iron have been classified by Walters, Catalán, Goudsmit, and put in a final form by Laporte *. The constitution of the spectrum is in many respects similar to that of chromium, which was first classified by Catalán †. Both consist of triplets, quintets, and septets with inter-combinations among the different systems. In both spectra many chief terms belong to the quintet system. For convenience of reference they are diagrammatically represented in Charts 1 and 2.

CHART 1.

Spectrum of Iron.

The Quintet System.

n^5_{30}	n^5_{31}	n^5_{32}	n^5_{33}	n^5_{34}	n^5_{41}	n^5_{42}	n^5_{43}	n^5_{44}	n^5_{45}	n^5_{51}	n^5_{52}	n^5_{53}	n^5_{54}	n^5_{55}	Term value.	Laporte's notation.
		n^5_{12}													$x-39713$	$\bar{s}$
	n^5_{21}	n^5_{22}	n^5_{23}													
		−263·7	−413·0												$x-29056$	p^1
		−252·0	−390·6												$x-36766$	p^2
		−219·2	−327·0												$x-42532$	p^3
		−200·0	−177·0												$x-16372$	p
− 89·9	−184·1	−288·1	−415·9												$x-68000$ (?)	d^1
− 71·1	−139·7	−199·5	−240·2												$x-25900$	$\bar{d}^1$
−104·5	−215·5	−294·4	−411·2												$x-33095$	$\bar{d}^2$
− 86·7	−173·2	−261·5	−344·0												$x-39625$	$\bar{d}^3$
− 86·0	−175·3	−273·6	−384·3												$x-44677$	d^2
					−168·9	−257·7	−351·3	−448·5							$x-6928$	$\bar{f}^1$
					−106·8	−164·9	−227·9	−292·3							$x-26874$	f^1
					−144·9	−218·4	−289·2	−344·1							$x-33695$	f^2
					−112·3	−176·0	−247·7	−337·1							$x-40257$	f^3
															$x-34782$	$\bar{g}^1$
															$x-42912$	$\bar{g}^2$

* Laporte, *Zeits. für Physik*, vol. xxiii. p. 135, and vol. xxvi. p. 1. All the other references will be found there.

† *Vide* Gieseler, *Zeits. für Physik*, vol. xxii. p. 228 (1924).

Constitution of the Spectrum of Iron.

The spectrum of iron as investigated by Laporte has been shown to consist of septets, quintets, and triplets, and each system consisting of parallel sets of "undashed" and "dashed" terms. The notation is that of Landé *.

The highest terms so far obtained are five-fold d -terms of the quintet system. As the term values are not known with certainty, the largest term, d_4^1, is denoted by x. The other d^1's are obtained by adding (in the algebraic sense) the corresponding frequency difference to d_4^1. Thus

$$d_3^1(n_{33}^5)=x-415{\cdot}9,\quad d_2^1(n_{32}^5)=d_3^1-288{\cdot}1.$$

The negative value of the frequency difference shows that the terms are "Verkehrte" or "inverse."

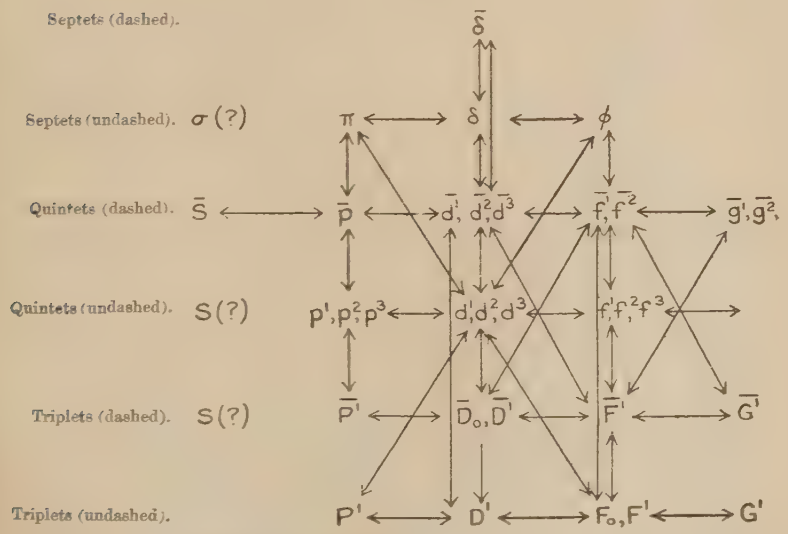
The next highest term is f_5^1, which is equivalent to $x-6928$. The next set is $\bar{F}^1$ of the triplet system, $\bar{F}_3^1=x-11976$.

Lines having $\bar{d}^1$'s and $\bar{f}^1$'s as initial terms have come in absorption on certain plates only.

The combinations are represented in the following modified Laporte diagram (called henceforth "Key to the Iron-Spectrum") :—

Fig. 3.

Key to Iron Spectrum.



* *Zeitschrift für Physik*, vol. xv. p. 191 (1923).

A glance at the chart shows that a term, say d^1, combines with those indicated by arrows, viz. with d^1, $\bar{d}^2$, $\bar{d}^3$; p^1, p^2, p^3 ; f^1, f^2, f^3 ; D_0, $\bar{D}^1$; π, ϕ, P^1, F_0, F^1 ; and breaks the selection principle of combining with g^1, $G^{\bar{1}}$, which is not shown in the chart. Similar remarks apply to every term shown in the key-diagram.

CHART 2.

Spectrum of Chromium.

The Quintet System.

						Term value.	Catalán's* notation.
		n^5_{12}				46948·48 ...	$1s^a$
	n^5_{21}	n^5_{22}	n^5_{23}				
	−5·75	−8·76				27754·69 ...	$2p^a$
	163·7	239·9				24717·86 ...	$2p^c$
	52·6	60·6			Rydberg sequence	13499·30 ...	$3p^c$
	7·8	15·5				9164·98 ...	$4p^c$
n^5_{30}	n^5_{31}	n^5_{32}	n^5_{33}	n^5_{34}			
60·00	116·50	167·69	212·72			46233·96 ...	d^a
86·0	118·4	129·4	144·6		Dashed system	20824·9 ..	d^b
64·5	119·7	166·3	207·0			13516·2 ...	d^c
	n^5_{41}	n^5_{42}	n^5_{43}	n^5_{44}	n^5_{45}		
	71·4	106·6	141·0	174·0		23262·10 ...	f^a
	64·9	114·7	138·7	168·8		13149·2 ...	f^b

* Catalán, *Ann. Soc. Espan. Fis. y. Chim.* vol. xxi. p. 84 (1923).

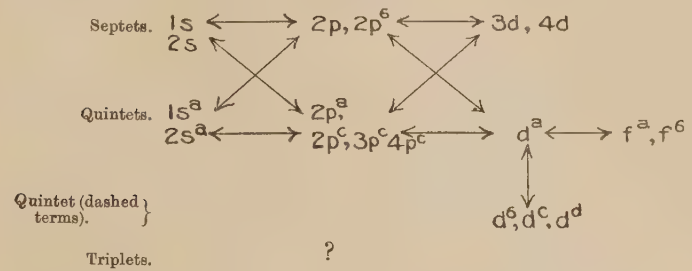
Constitution of the Spectrum of Chromium.

The spectrum of chromium consists of septets, quintets, and triplets. The highest term so far obtained is an $1s$-term of the septet system, *i. e.* n^7_{13}, having the value 54511·26. The septet lines $1s-2p$, $1s-2p^b$ constitute the strongest lines of the chromium spectrum, and were the only lines obtained by Gieseler and Grotrian in absorption in the furnace. They did not get even the $1s^a-2p^a$ terms of the quintet system in absorption.

The quintet system of chromium has a $1s$-term, *i. e.* n^5_{12} having the value 46948·48. But this value is approached by 5-fold d^a-terms, n^5_{34} being 46233·96. According to our view, this corresponds to the 5-fold d^1-terms of iron, which are the highest terms obtained by Laporte (d^4_1 in Laporte's notation).

The combinations of chromium are represented in the following Laporte diagram. The values are taken from Gieseler's * paper.

Fig. 4.



Comparison of the Spectra of Chromium and Iron.

A comparative study of the two charts shows that the greater complexity of the iron spectrum is entirely due to the full development of the "gestrichene" or the "dashed" system. These are only feebly developed in chromium (d^b, d^c, d^d).

The question still remains open whether the quintet or septet system of iron may not contain a 1*s*-term larger than the d^1's.

Analysis of Table I.

From analysis of Table I. we find that the following system of lines have been obtained in absorption :—

(*a*) Multiplets having d^1's as initial orbits (*vide* key to iron spectrum).

Multiplet 1. d^1-p^1, all lines obtained excepting $d_2^1-p_3^1$.
„ 2. d^1-p^2, all lines.
„ 3. $d^1-\bar{d}^1$, „
„ 4. $d^1-\bar{d}^2$, „
„ 5. $d^1-\bar{d}^3$, 9 lines out of 12 obtained.
„ 6. d^1-f^1, all lines.
„ 7. d^1-f^2, all lines except $d_2^1-f_1^2$.
„ 24. $d^1-\bar{D}^1$, very weak lines; 5 out of 9 obtained.

See under :

Multiplet 24. d^1-F^1. only 3 lines.
„ 23. d^1-P^1, only 2 strongest out of 7 lines obtained.
„ 46*a*. $d^1-\bar{g}^1$, only 3 out of 9 obtained.
„ 46*b*. $d^1-\bar{G}^1$, only 2 lines obtained.

* Gieseler, *Zeits. f. Phys.* vol. xxii. p. 228 (1924).

The last two are rather remarkable as the lines are weak, and, as pointed out by Laporte, break the principle of selection.

(*b*) Multiplets having the next terms $\bar{f}^1$ as their initial orbits.

Multiplet 10. $\bar{f}^1-\bar{d}^2$, 8 out of 12 lines obtained.
,, 11. $\bar{f}^1-\bar{d}^3$, 8 out of 12 lines obtained.
,, 13. $\bar{f}^1-f^2$, 9 out of 13 lines obtained.
,, 14. $\bar{f}^1-f^3$, only the strongest line obtained.
,, 15. $\bar{f}^1-\bar{g}^1$, partially explored; only 2 lines obtained.
,, 26. $\bar{f}^1-\bar{G}^1$, only 2 strongest out of 8 lines obtained.
,, 47. $\bar{f}^1-\bar{g}^2$ *?, 9 out of 11 lines obtained.

* Multiplet 47 was provisionally classified by Laporte to belong to f^1-g^2 combinations. The absorption experiment completely establishes the validity of the classification.

The line $f^1-\bar{P}^1_2$ which breaks the principle of selection has also been obtained in absorption.

(*c*) On some plates, lines having the next highest terms F^1 of the triplet system have come out in absorption. This is reproduced in the plate.

Multiplet 20. $\bar{F}^1-\bar{D}^1$, all lines obtained except the two weakest.
,, 21. $\bar{F}^1-F^1$, the plate contains 3 lines out of 7.
,, 22. $\bar{F}^1-\bar{G}^1$, no plate taken.

No other lines have come out in absorption.

According to Laporte's classification, d^1, $\bar{f}^1$, $\bar{F}^1$ form the successive highest groups of terms. It is noteworthy that while on all plates lines having $\bar{d}^1$'s and $\bar{f}^1$'s have come out in absorption, though the $\bar{f}^1$-combinations have come out rather faintly. The strong group of lines represented by the triplet combinations :

$\bar{F}^1-\bar{D}^1$, strongest line, $\bar{F}^1_4-\bar{D}^2_1$, $\lambda=3815{\cdot}84$ (100*r*),
$\bar{F}^1-F^1$, strongest line, $\bar{F}^1_4-F^1_4$, $\lambda=4045{\cdot}82$ (60*r*),
$\bar{F}^1-\bar{G}^1$, strongest line, $\bar{F}^1_4-\bar{G}^1_5$, $\lambda=4271{\cdot}76$ (35),

have come in absorption only on a few plates. On some plates they were obtained as emission lines.

None of the lines having the next highest terms d^1 have come out in absorption, while much less intense lines having d^1's as their initial terms have been obtained in absorption.

We may refer to the group $\bar{d}^1 - \bar{g}^1$, which break the selection-principle, for here we have the azimuthal quantum number changing from 3 to 5.

$\lambda = 2874{\cdot}18$ intensity 10 (I), $d_4^1 - \bar{g}_5^1$.

$\lambda = 2869{\cdot}31$ intensity 10 (I), $d_3^1 - \bar{g}_5^1$.

One is reminded of Datta's work on the absorption spectrum of potassium vapour in which faint $1s - md$ lines were obtained in absorption, but no $2p - md$ or $2p - ms$ lines, though in the emission spectrum the latter are much more intense. The analogy is quite complete.

The work thus confirms the validity of Laporte's classification of iron lines, but many absorption lines obtained still remain unclassified.

The potentiality of the method for studying the absorption spectra of elements seems to be very great, and if spectroscopes with greater resolving and light-gathering power are available, the water-spark can be made to give very good absorption spectra.

Ionization Potential of Iron.

It may be mentioned in this connexion that on the basis of this and other absorption experiments, it is probably not safe to conclude that the d^1's are the fundamental orbits of Fe.

For this purpose, the charts on the spectra of Fe and Cr may be compared. In chromium the highest term is $1s$ of the septet system, and the next is $1s^a$ of the quintet system. The d^a-terms of the quintet group of chromium give a very important set of lines in the chromium spectrum, and are thus analogous to the d^1-group of iron. But in the iron spectrum no term corresponding to the $1s$, $1s^a$ of chromium have been obtained. These are marked with a query mark in the key to the iron spectrum.

The question arises if, in the case of iron, $1s$-terms exist, and, if so, whether they have larger values than the d^1's. Gerlach * reports that some extraordinarily strong iron lines have been obtained in the water-spark between $\lambda = 2000$ to $\lambda = 2100$ A.U., and that these lines could not be fitted into Laporte's scheme. Unfortunately we have not been able to study this region with our apparatus. In the case of Cr, Gieseler and Grotrian † investigated the absorption spectrum

* Gerlach, *Physik. Zeitschr.* vol. xxv. p. 620 (1824), and *Ann. der Physik*, vol. lxxvi. p. 197 (1925).

† Gieseler and Grotrian, *Zeits. f. Phys.* vol. xxii. p. 245 (1924).

in the furnace at 1250° C., but got only $1s - mp$ lines. No line beginning with $1s^a$ or d^a's were obtained in absorption. In the case of iron, on the other hand, the strong group $d^1 - \bar{d}^1$ was obtained in absorption at 1250° C., so that this experiment may be interpreted as deciding against the existence of a higher 1*s*-term. But we do not hold this sort of evidence to be decisive, because at the high temperature of the furnace it is quite possible that a large fraction of d^1-orbits are produced. Once they are produced they will remain fairly stable, for the transition $d \rightarrow s$ being forbidden, the *d*-states will be metastable. This is supported by evidence from the chromospheric spectrum. The strongest lines in the iron spectrum,

$$\lambda = 3856{\cdot}46 \text{ Å.U. } d_3^1 - \bar{d}_2^1, \quad \lambda = 3860{\cdot}01 d_4^1 - \bar{d}_4^1,$$

reach in the solar chromosphere a height of 6000 km., and Evershed* notes that they are intensified from intensity 8 (Rowland's scale) in the Fraunhofer spectrum to 15 in the flash spectrum. This behaviour is typical of lines arising from metastable orbits. If the higher 1*s*-term exists at all, the value will be in the neighbourhood of 80,000, corresponding to an ionization potential about 10 volts. This point and other points mentioned in the paper are receiving attention.

Summary.

The paper describes an experimental work on the absorption spectrum of iron, which is obtained when the high-frequency spark produced between two iron electrodes immersed in distilled water is analysed by a spectroscope. The exact experimental conditions are described in detail, and the results obtained are compared with the recent work of Laporte on the classification of iron lines. It is shown that all multiplets having the three highest groups of terms, viz. d^1, f^1 and occasionally $\bar{F}^1$, as initial orbits, are obtained in absorption. Some weak lines are also obtained in absorption which are shown to correspond to the transition of the azimuthal quantum number from k to $k+2$ (violation of Sommerfeld's selection-principle). It is shown that this method of obtaining absorption spectra is as suitable as the more elaborate method of obtaining it in the furnace. Arguments are advanced in support of the view that iron may have a term higher than the *d*-term which is the highest so far obtained.

I take this opportunity of recording my sincere thanks to Prof. M. N. Saha for his guidance and interest in the work.

* Evershed, Phil. Trans. vol. cci. p. 474 (1901).

XXXVI. *On the Absorption Spectra of Aluminium and Cobalt.* *By* N. K. Sur, *M.Sc*, *and* K. Majumdar, *M.Sc.*, *Department of Physics, University of Allahabad* *.

Introductory.

It is generally acknowledged that the study of the absorption spectra of elements provides us with the simplest method of determining the normal states of atoms, and thus affords a clue to the analysis of their spectra. The first systematic study was made by Wood † and Bevan ‡, and afterwards corroborated in certain cases by McLennan §. They proved that in the case of elements of the first and second groups the normal orbits are those designated spectroscopically by 1*s* and 1S respectively.

The subject has acquired great importance in connexion with the classification of series spectra of the group of elements from Sc to Ni and of the elements of the third group. A few years ago it was believed from analogy that, in the case of every element, the lowest energy level corresponded to a 1S-term, having the azimuthal quantum number 1 and radial quantum number 0. But it was found from analysis of the spectra of metals of the third group that the largest series term was in every case a $2p$-term ‖. This fact was also corroborated by the absorption experiments of Grotrian ¶, Carroll **, and Narayan ††; in the case of thallium, indium, and gallium, they showed that the first lines to come out in absorption at the lowest temperatures were $2p_2$–ms and $2p_1$–ms.

Similar absorption experiments have been carried out in the case of the elements Sc, Ti, Va, Cr, Mn, and Fe by Grotrian and Gieseler ‡‡, and in certain cases by Angerer and Joos §§. They have obtained results which are quite subversive of the earlier notions (viz. in every case the highest term is 1S), but which generally support the results obtained

* Communicated by Prof. M. N. Saha.

† Wood and Fortrat, Astrophys. Journ. vol. xliii. p. 73 (1916).

‡ Bevan, Proc. Roy. Soc. Lond. A, vol. lxxxiii. p. 421, vol. lxxxv. p. 54 (1910).

§ McLennan and Ireton, Phil. Mag. vol. xxxvi. p. 461 (1918); McLennan, Proc. Phys. Soc. Lond. vol. xxxi. p. 1 (1918).

‖ Fowler, 'Report on Series Spectra,' chap. xvii.

¶ Grotrian, *ZS. f. Phys.* vol. xii. p. 218 (1922).

** Carroll, Proc. Roy. Soc. Lond. A, vol. ciii. p. 334 (1923).

†† Narayan, Proc. Roy. Soc. Lond. A, vol. cvi. p. 596 (1924).

‡‡ Grotrian and Gieseler, *ZS. f. Phys.* vol. xxv. pp. 165, 342 (1924).

§§ Angerer and Joos, *Ann. d. Phys.* vol. lxxiv. p. 743 (1924).

from straightforward analysis of the spectra of these elements, carried out recently by Catalán, Kiess and Kiess, Meggers, Laporte, and others. These results are summarized below in Table I.

TABLE I.

Element.	Designation.	Landé's symbol.	Remarks.
19 K	1*s*	n_{11}^2	
20 Ca ...	1S	n_{10}^1	
21 Sc ...	D or P?	n_{22}^2 or n_{33}^2	Catalán and Grotrian, *Zeits. f. Phys.* xxv. p. 362 (1924).
22 Ti.....	*f*	n_{44}^3	Kiess and Kiess, Journ. Opt. Soc. Am. viii. p. 607 (1924).
23 Va ...	F	n_{45}^4	Bechert and Sommer, *Zeits. f. Phys.* xxxi. p. 158 (1925).
24 Cr ...	1*s*	n_{13}^7	Gieseler, *Zeits. f. Phys.* xxvi. p. 228 (1924).
25 Mn ...	1S	n_{14}^8	Catalán, Phil. Trans. Roy. Soc. Lond. ccxxiii. p. 127 (1922). Landé, *Zeits. f. Phys.* xv. p. 191 (1923).
26 Fe ...	*d*	n_{34}^5	Laporte, *Zeits. f. Phys.* xxiii. p. 135 (1924).
27 Co ...		n_4^4	Catalán and Bechert, *Zeits. f. Phys.* xxxii. p. 336 (1925).

The above summary shows that it is almost hopeless to deduce any general conclusion regarding the quantum specification of the normal orbits. Only Cr and Mn behave in a normal way, *i. e.* the 1*s*-terms are the largest. But in other cases 2*p*-, *d*-, or even *f*-terms have been found to be the highest.

The investigations reported below were undertaken in order to make a systematic study of the whole range of phenomena from the following standpoints :—

(1) To study the absorption spectra of elements which are still unknown, and thus obtain a clue to their constitution ; and

(2) To study the variation of the absorption spectra under different temperatures and pressures, and thus make a systematic study of the production of higher orbits.

Thus at the lowest temperature Na vapour absorbs only 1*s*–*mp* lines. The problem before us is to find out at what temperature it will begin to absorb 2*p*–*ms*, or *md*-lines, and in what proportion ?

King * has found that the $2p$-orbits of Na are produced in sufficient quantity only at temperatures of 2000° C., while experiments carried out in this laboratory show that a temperature of 1250° C. is generally sufficient. Grotrian and Gieseler † have found that if there is a set of orbits very close to the lowest orbits, as is generally the case with the higher elements, the absorption spectra that arise generally consist of lines proceeding from both sets, and it is not possible to mark out a stage when only one class appears in absorption to the exclusion of the next. Thus, in the vanadium spectrum, the lowest level is the F′-term of the quartet system, the next level being given by $\bar{d}'$ of the sextet system. But the difference between the two sets is only $\Delta\nu = 2112{\cdot}5$. In the absorption spectra lines with F′ and $\bar{d}'$, combinations come out simultaneously and almost with the same strength. Thus the absorption spectra lose much of their pristine simplicity, and become more complex than desirable.

We have, therefore, designed an apparatus in which the temperature, as well as the quantity of material, could be varied continuously. We have first studied the absorption spectra of aluminium, cobalt, and nickel. Aluminium was chosen because its absorption spectrum had not yet been obtained. Cobalt and nickel were chosen because they are the only elements in the third horizontal row of the periodic table of which the series classifications were still unknown. Results obtained with Al and Co are reported below.

Apparatus.

The metal was vaporized within a vacuum furnace of the type designed first by King and used subsequently by Saha ‡, Grotrian, and others. A sketch of the furnace is given in fig. 1.

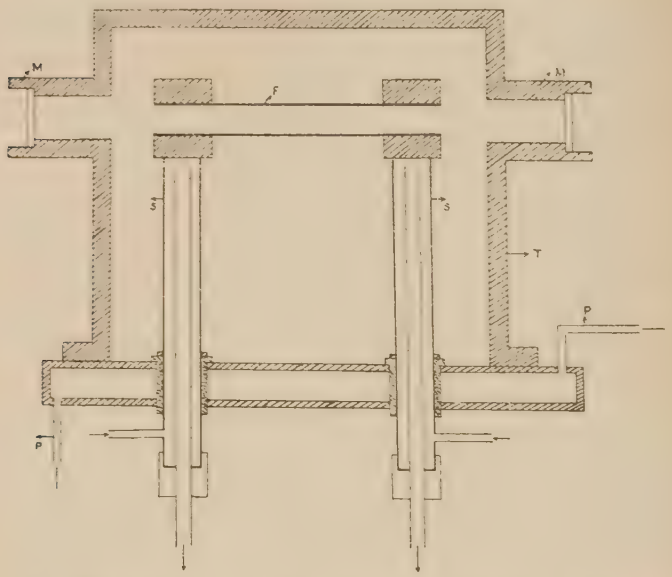
Description of the Furnace.

The furnace consists of a thin tube F of Acheson graphite, which was heated by a current taken from a set of heavy-discharge accumulators. We used 5 cells, and the voltage across the terminals was found to be 8·5 volts instead of 10. The loss is due to the resistance in the connecting leads, which consisted of thick copper wires enclosed within hose-pipes through which water was kept circulating. The current was taken through two parallel pools of mercury, and contact was made by a thick sliding copper piece. This served the

* King, Astrophys. Journ. vol. lv. p 354 (1922).
† Grotrian and Gieseler, *ZS. f. Phys.* vol. xxv. p. 342 (1924).
‡ Saha and Sur, Journ. Ind. Chem. Soc. vol. i. p. 9 (1924).

double purpose of a switch as well as an adjustable resistance. By sliding the contact piece along the pools of mercury, the terminal voltage could be reduced to any value. The highest temperature obtained was 2100° C. The current, on measurement, was found to be 680 amperes.

Fig. 1.



The construction of the furnace is apparent from the diagram. There was a side tube (not shown) which was closed by means of a quartz plate. Temperature could be measured by means of a Wanner pyrometer placed on this side. This was calibrated by Mr. Kampta Prasad by taking the melting-points of NaCl and Cu as standards. The furnace was shielded by a concentric iron mantle with a hole facing the quartz window.

Spectroscopic Arrangement.

Continuous light from a copper water-spark was rendered parallel by means of a quartz lens and allowed to traverse the furnace. The beam was then focussed on the slit of a concave grating which has a radius of 5 feet and a ruled surface of 1·5 inches. The mounting is of the Rowland type, giving a dispersion of 11·11 Å.U. per mm. in the first order. Some photographs were taken in the second order as well.

The source of continuous light was a high-frequency oscillatory spark between copper electrodes immersed in

distilled water. The principal lines of copper $\lambda=3273{\cdot}95$, $\lambda=3247{\cdot}55$ always came on the continuous background as absorption lines, and served as fiducial points. The source was so bridiant that an exposure of 1–2 minutes was quite sufficient for the first-order spectrum.

Aluminium.

As has been already mentioned, Grotrian has corroborated by absorption experiments that in the case of indium, gallium, and thallium the $2p$-orbit is the normal state. His absorption experiments with Al were not fruitful, as he used silica tubes closed by quartz plates, which are strongly attacked by Al at high temperatures. Moreover, Al yields very little vapour up to 1200° C. By using the graphite furnace and heating it up to 1520° C., the pair

$$\lambda=3961{\cdot}54 \text{ and } \lambda=3944{\cdot}03\ (2p–2s)$$

came out reversed. At 1650° C. the leading members of $2p–md$ series were obtained in reversal, and at 1725° C. the second pair of $2p–ms$ series was also obtained in absorption. It may be mentioned that on all plates the lines at $\lambda=2874{\cdot}24$ and $\lambda=2450{\cdot}10$ belonging to the $2p–md$ series of gallium, and the line at $\lambda=4172{\cdot}06$ of the $2p–ms$ series were also obtained in absorption.

TABLE II.

Aluminium lines obtained as reversals.

(λ.)	Series notation.
Sharp Series.	
3961·54	$2p_2-2s$
3944·03	$2p_2-2s$
2660·39	$2p_1-3s$
2652·48	$2p_2-3s$
Diffuse Series.	
3092·84, 92·72	$2p_1-3d_i$ (i=1 or 2 not resolved)
3082·16	$2p_2-3d_2$
2575·41, 75·11	$2p_1-4d_i$
2567·99	$2p_2-4d_2$
2373·36, 73·13	$2p_1-5d_i$
2367·06	$2p_2-5d_2$
2269·21, 69·05	$2p_1-6d_i$
2263·45	$2p_2-6d_2$
2210·05	$2p_1-7d_i$ (on one plate only)

As the photographs were taken in the first-order spectrum of the concave grating, the dispersion was not sufficient to separate the $2p_1–md_1$ and $2p_1–md_2$ lines of the diffuse series.

A line at $\lambda = 3057{\cdot}16$ was also obtained on one plate, but we could not trace it to its source.

From this experiment it results that the lines which appear in absorption belong to the subordinate series of aluminium, for which the $2p$-terms represent the initial states.

It must be mentioned here, however, that it is not possible to deduce from such experiments whether, for aluminium, the $2p$-terms represent the normal orbits or not. For, at the temperature at which sufficient vapour is available for absorption experiments, the thermal stimulus is high enough to convert an appreciable fraction of possible $1s$-orbits to the $2p$-stage. A positive answer can be given by simultaneous measurement of the vapour-pressure of aluminium, which is still unknown, and from measurement of the dispersion of Al vapour, which will give the number of centres of absorption, *i. e.* atoms in $2p$-orbits. If the ratio of the number of absorption centres to the number of atoms present be of the order unity, then and then only we can maintain that $2p$ is the normal state of Al-atoms. Such experiments have been done by Ladenburg and Loria * in the case of hydrogen (excited by electric spark), who found that 1 in 50,000 of the atoms are excited to the $2p$ orbit, and by Hallo † and Geiger ‡ in the case of Na, who found that 1 atom in 12 can act as absorption centres for D_1 and D_2. This shows that D_1 and D_2 arise from normal orbits, while $H\alpha$ of hydrogen arises from a higher orbit.

Note.—It may be worth recording in this connexion that in attempting to study spectroscopically the thermal ionization of calcium vapour, a rather interesting fact was observed. At about 800° C., the g-line of Ca is not obtained in absorption, though the vapour-pressure is quite sufficient. A band spectrum was obtained extending roughly from 3150 Å.U. to 4100 Å.U. At low temperatures, Ca and probably the other alkaline earths are in a diatomic state. This is also confirmed by the vapour-pressure experiments of Ruff and Hartmann (vide *Zeits. für Anorg. und Allg. Chemie*, cxxxiii. pp. 29–45, 1924). They have found from vapour-pressure data that the chemical constant has a value which is abnormally high, if we suppose Ca to be monatomic. According to Nernst's theory, $C = -1{\cdot}62 + \frac{3}{2}\log M$. Taking $M = 40$, the chemical constant of monatomic calcium ought to be 0·78, while Ruff and Hartmann find it to be 3·44. This indicates that at a temperature of 800° C., calcium is diatomic, while at higher temperatures it is broken up into atoms.

* Ladenburg and Loria. *Verh. d. D. Phys. Ges.* vol. x. p. 858 (1908).
† Hallo, *Phys. Zeits.* vol. iv. p. 545 (1903).
‡ Geiger, *Ann. d. Phys.* vol. xxiv. p. 597 (1907).

Cobalt.

Angerer and Joos have performed absorption experiments with cobalt in a different type of furnace. The lines obtained by them are marked "A" under the heading "Remarks" in Table III., in which the wave-length of lines of cobalt

TABLE III.

Absorption lines of Cobalt in the furnace.

Wave-length I.A. (Dhein).	Wave-number (vacuum).	Intensity and class (King).	Series classification (Catalán & Bechert *).	Multiplet number (Catalán & Bechert).	Remarks.
4190·709	23855·61	20 I	$f_5^1 - \bar{\phi}_5^1$	71	
4076·134	24526·15	3 Ia	$f_3^2 - \bar{f}_3^1$	28	
4027·044	24825·12	10 I	$f_3^1 - r_4^1$	73	
3997·909	25006·03	40 II	$F_3^1 - f_4^2$	64	
3995·312	25022·08	60 II	$F_4^1 - g_5^2$	67	
3961·006	25238·99	6 II	.....	...	not classified
3945·323	25339·32	15 I	$F_4^1 - F_3^1$	6	
3909·941	25568·62	15 I	$f_5^1 - r_6^1$	73	
3894·981	25666·82	20 II	$f_2^2 - d_1^1$	22	just separated
3894·086	25672·72	60 II	$F_3^1 - G_4^2$	9	just separated
3873·957	25806·10	40 II	$f_4^2 - d_3^1$	22	
3873·117	25811·70	60 II	$f_5^2 - d_5^1$	22	
3845·474	25997·24	60 II	$F_4^1 - G_5^2$	9	
3745·501	26691·14	25 I	$F_4^1 - G_4^2$	9	
3631·340	27530·23	20r II	$f_4^1 - \bar{f}_5^1$	25	
3627·807	27557·03	25r I	$f_4^2 - G_5^1$	58	
3624·955	27578·71	8 I	$f_2^2 - d_3^2$	23	
3604·469	27735·45	4 II	.....	...	not classified
3602·081	27753·84	40R II	$f_2^1 - \bar{f}_2^1$	25	
3594·869	27809·52	50R II	$f_3^1 - \bar{f}_3^1$	25	
3585·159	27884·84	20R I	$f_4^2 - d_4^2$	23	not resolved
3584·796	27887·66	15 I	$f_3^1 - d_4^1$	19	not resolved
3575·361	27961·25	60r II	$f_4^1 - \bar{f}_4^1$	25	
3574·964	27964·36	25r I	$f_3^2 - d_3^2$	23	
3569·382	28008·10	80R II	$F_4^1 - \bar{F}_4^2$	7	
3564·955	28042·87	25r I	$f_3^2 - G_4^1$	58	
3560·896	28074·83	20r I	$f_2^2 - d_2^2$	23	
3533·363	28296·60	25r I	$f_2^1 - g_3^1$	31	

* Catalán and Bechert, *Zs. f. phys.* vol. xxxii. pp. 336–369 (1925).

TABLE III. (*continued.*)

Wave-length I.A. (Dhein).	Wave-number (vacuum).	Intensity and class (King).	Series classification (Catalán & Bechert).	Multiplet number (Catalán & Bechert).	Remarks.
3529·815	28322·03	80R II	$f_4^2 - g_5^2$	35 } ...	A just resolved
3529·037	28325·06	30R I	$f_3^1 - g_4^1$	31 }	
3526·856	28345·79	100R II	$f_5^1 - \bar{f}_5^1$	25.....	A
3523·438	28373·28	25*r* I	$f_2^2 - d_1^2$	23	
3521·572	28388·32	30*r* I	$f_5^2 - \mathrm{F}_4^1$	54	
3520·087	28400·29	15 I	$f_4^1 - f_3^1$	25	
3518·353	28414·29	50R II	$\mathrm{F}_3^1 - \mathrm{D}_2^2$	5	
3513·483	28453·68	50R II	$f_4^1 - g_5^1$	31	
3512·643	28460·49	60R II	$f_3^2 - d_2^2$	23	
3510·419	28478·52	30*r* I	$f_4^1 - d_4^1$	19 } ...	A not resolved
3509·844	28483·19	50*r* II	$f_3^2 - g_4^2$	35 }	
3506·315	28511·85	80R II	$f_4^2 - d_3^2$	23	
3502·281	28544·69	100R II	$f_5^2 - d_4^2$	23.....	A
3495·685	28598·53	50*r* II	$f_2^2 - g_3^2$	35	
3491·324	28634·27	15 I	$f_2^1 - d_2^1$	19 }	not resolved
3490·741	28639·04	10 I	$f_4^2 - \bar{\mathrm{F}}_3^1$	54 }	
3489·406	28650·00	60*r* II	$\mathrm{F}_4^1 - \mathrm{D}_3^2$	5	
3483·415	28699·28	20*r* I	$f_4^2 - f_5^2$	29	
3474·019	28776·90	100R II	$f_3^2 - f_4^2$	29.....	A
			$f_5^1 - f_4^1$	25.....	A
3465·796	28845·18	100R II	$f_5^1 - g_6^1$	31.....	A
3462·807	28870·07	60*r* II	$f_2^2 - \bar{f}_3^2$	29	
3453·513	28947·75	200R II	$f_5^2 - g_6^2$	35.....	A
3449·443	28981·91	60R II	$f_5^2 - g_5^2$	35 }	not resolved
3449·171	28984·20	60R II	$f_3^2 - g_3^2$	35 }	
3443·646	29030·70	80R II	$f_4^2 - g_4^2$	35.....	A
3433·043	29120·36	60R II	$f_2^2 - \bar{f}_2^2$	29	
3412·636	29294·48	80R II	$f_5^1 - d_4^1$	19 } ...	A not resolved
3412·335	29297·07	80R II	$f_4^2 - \mathrm{G}_5^2$	59 } ...	A
3409·176	29324·21	60*r* II	$f_4^2 - \bar{f}_4^2$	29	
3405·120	29359·15	150R II	$f_5^2 - \bar{f}_5^2$	29.....	A
3395·378	29443·38	40*r* II	$f_3^2 - \mathrm{G}_4^2$	59	
3385·227	29531·67	25*r* II	$f_4^2 - g_3^2$	35	
3367·114	29690·52	30*r* II	$f_5^2 - g_4^2$	35	
3354·386	29803·17	20R II	$f_4^2 - \bar{f}_3^2$	29	
3334·151	29984·05	30*r* II	$f_5^2 - \bar{f}_4^2$	29	

TABLE III. (*continued*).

Wave-length I.A. (Dhein).	Wave-number (vacuum).	Intensity and class (King).	Series classification (Catalán & Bechert).	Multiplet number (Catalán & Bechert)	Remarks.
3249·994	30760·44	6 II	$f_3^2 - \bar{F}_4^2$	55	
3247·176	30787·13	8 II	.....	...	not classified
3159·660	31639·84	10 II	$f_3^2 - \bar{F}_3^2$ / $f_2^1 - d_1^2$	55, 20	not clearly separated
3158·769	31648·78	12 II	$f_4^1 - g_5^2$	32	
3147·060	31766·51	15*r* II	$f_3^1 - g_4^2$	32	
3137·325	31865·08	10 II	$f_2^1 - g_3^2$	32	
3121·560	32026·01	12R II	$f_4^1 - f_5^2$	26	not resolved
3121·414	32027·51	12R II	$f_5^1 - d_4^2$	20	
3072·346	32538 99	15*r* II	$f_3^1 - \bar{f}_3^2$	26	
3064·375	32623·62	5 II	$f_4^1 - G_5^2$	57	
3061·825	32650 80	20*r* II	$f_4^1 - \bar{f}_4^2$	26	
3048·892	32789·29	12*r* II	$f_3^1 - \bar{f}_2^2$	26	
3044·007	32841·91	30R II	$f_5^1 - \bar{f}_5^2$	26.....	A
3034·426	32945·59	6 II	$f_3^1 - D_2^1$	48	
2987·172	33466 74	15*r* II	$f_5^1 - \bar{f}_4^2$	26	

Wave-length I.A. (Dhein).	Wave-number (vacuum).	Intensity (Dhein).	Series classification (Catalán & Bechert).	Multiplet number (Catalán & Bechert).	Remarks.
2842·388	35171·37	3	.....	...	not classified
2833·928	35276·36	1	$f_4^1 - D_3^2$	49	
2814·979	35213·81	2	$f_4^1 - \bar{F}_3^2$	53	
2663·531	37533·00	4	.....	...	not classified
2650·271	37720·77	4	$f_2^2 - \bar{f}_2^3$	30	

Wave-length I.A. (Krebs).	Wave-number (vacuum).	Intensity (Krebs).	Series classification (Catalán & Bechert).	Multiplet number (Catalán & Bechert).	Remarks.
2574·366	38832·90	3R	$f_4^1 - d_4^3$	21	
2544·330	39291·28	2	$f_2^1 - d_1^3$	21.....	A
2528·968	39529·95	3R	$f_4^1 - d_3^3$	21.....	A
2424·938	41225·63	3R	$f_5^1 - \bar{f}_5^3$	27	
2407·260	41528·35	3R	$f_5^1 - g_6^3$	33.....	A
2354·825	42452·94	2	.....	.....	A not classified

obtained by us in reversal are noted. It will be seen that we have obtained more lines than Angerer and Joos *. On the short wave-length side the work is not yet complete. The graphite tube was heated to 1950° C. or 2000° C. Apparently, cobalt does not give sufficient vapour at lower temperatures. The wave-lengths are taken from the measurements of Dhein †.

Analysis of Table III.

After this work was completed, Catalán and Bechert published a paper ‡ in which the series classification of cobalt lines has been worked out. From a comparison of our data with Catalán's work, we find that lines belonging to the following multiplets have been obtained in absorption. We also append a key of the cobalt spectrum for explaining the combinations :—

(*a*) Lines belonging to multiplets having f^1 as initial orbits :—

Multiplet 19, f^1d^1—four lines obtained.
,, 20, f^1d^2—two ,, ,,
,, 21, f^1d^3—three ,, ,,
,, 25, $f^1\bar{f}^1$—seven ,, ,,
,, 26, $f^1\bar{f}^2$—six ,, ,,
,, 27, f^1f^3—one line ,,
,, 31, f^1g^1—four lines ,,
,, 32, f^1g^2—three ,, ,
,, 33, f^1g^3—one line ,,
,, 48, f^1D^1— ,, ,,
,, 49, f^1D^2— ,, ,,
,, 53, $f^1\bar{F}^2$— ,, ,,
,, 57, f^1G^2— ,, ,,
,, 71, $f^1\phi^1$— ,, ,,
,, 73, $f^1\gamma^1$—two lines ,,

(*b*) Lines belonging to multiplets having f^2 as initial orbits :—

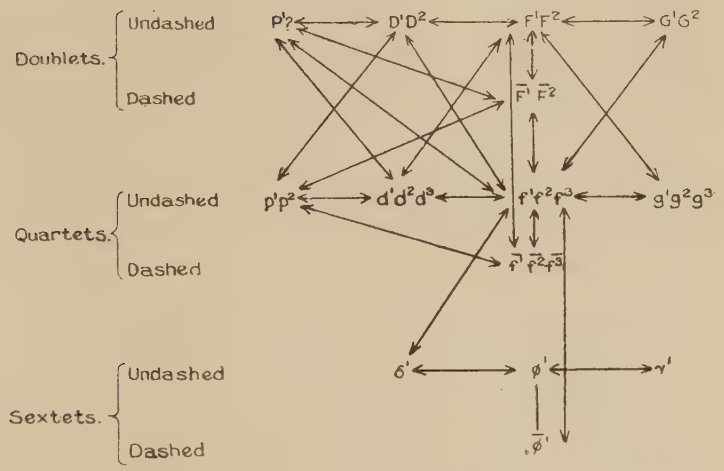
Multiplet 22, f^2d^1—three lines obtained.
,, 23, f^2d^2—eight ,, ,,
,, 28, f^2f^1—one line ,,
,, 29, f^2f^2—eight lines ,,
,, 30, $f^2\bar{f}^3$—one line ,,
,, 35, f^2g^2—nine lines ,,
,, 54, $f^2\bar{F}^1$—two ,, ,,
,, 55, $f^2\bar{F}^2$— ,, ,, ,,
,, 58, f^2G^1— ,, ,, ,,
,, 59, f^2G^1— ,, ,, ,,

* Angerer and Joos, *Ann. d. Phys.* vol. lxxiv. p. 755 (1924).
† Dhein, Kayser-Konen's *Handbuch der Spectroskopie*, vol. vii.
‡ *Zs. f. Phys.* vol. xxxi. p. 336 (1925).

(*c*) Lines belonging to multiplets having f^1 as initial orbits:—

Multiplets 5, F^1D^2—two lines obtained.
„ 6, $F^1\bar{F}^1$—one line „
„ 7, F^1F^2— „ „ „
„ 9, F^1G^2—three lines „
„ 64, F^1f^2—one line „
„ 67, F^1g^2— „ „ „

Fig. 2.



Key to Cobalt Spectrum.

The different combinations as shown by the arrows in the above diagram have been obtained by Catalán and Bechert. According to them the term P^1 is uncertain. f^1, f^2, F^1 are the biggest terms.

Discussion of Results.

According to the classification of the arc-spectrum of cobalt by Catalán and Bechert, f^1, f^2, and F^1 form the three closely successive highest groups of terms. Lines belonging to the f^1 and f^2 groups have come out prominently in absorption, while a few strong lines belonging to the F^1 group have also been obtained. The absorption experiment definitely points to the fact that an *f*-term is the fundamental term of the cobalt arc-spectrum ; but it is to be noted here that this is not in agreement with Bohr and Stoner's scheme of the periodic system, according to which a *d*-term is to be expected as the fundamental term. It is not possible to decide

from this experiment whether f^1 or f^2 is the fundamental term ; f^1 or f^2 corresponds to two close levels, the difference in these term-values being about 3500^{-1} cm., and, at the temperature necessary for the absorption experiment, transitions to the orbits corresponding to f^1 and f^2 terms are equally probable, as is shown by the lines absorbed. A clue to this would probably be obtained by pushing the experiment further in the ultra-violet region.

The lines belonging to the group $f^1\bar{\phi}^1$ are intercombination lines, and Catalán and Bechert have suggested them to be the resonance lines ; but only one line, $\lambda=4190{\cdot}709$ (I.A.), of this group was obtained in absorption. This is the strongest line of the suggested system of resonance lines, and the other weaker lines lie on the longer wave-length side of this line. Photographs were taken in this region, but no other line could be obtained in absorption. It appears that the group of lines $f^1\bar{\phi}^1$ is not important enough to be regarded as the resonance lines.

Summary.

The paper contains an account of experimental work on the absorption spectra of aluminium and cobalt in the high-temperature furnace. The $2p_1$–$2s$, $2p_2$–$2s$ lines of Al do not come in absorption before a temperature of 1520° C. is reached. The higher members of *ps*- and *pd*-series are obtained in absorption at about 1700° C.

The absorption spectrum of cobalt has been photographed from 4500 Å.U. to 3000 Å.U. at a temperature of 2000° C. The lines have been identified by measurement, and tabulated according to the series classification of Catalán and Bechert. It is shown that many lines belonging to f^1 and f^2, and a few lines belonging to F^1 terms, which are the three successive largest terms, have been obtained in absorption. Only one line, $\lambda=4190{\cdot}709$, belonging to the group which Catalán and Bechert have suggested for the resonance lines has come out in absorption.

We take this opportunity to express our sincere thanks to Prof. M. N. Saha for his guidance and interest in the work.

XXXVII. *The Determination of Young's Modulus from Compression Tests on Circular Cylinders.* *By* F. E. Relton, *B.A., B.Sc., Building Research Station, Department of Scientific and Industrial Research* *.

THE present paper owes its genesis to the call for an explanation of certain anomalies in the behaviour of specimens under compressive loads. These anomalies, which were rendered visible by the use of translucent specimens, were more apparent than real, being nothing more than the fact that plane horizontal sections did not remain plane under load; but they served to show that the compression test, as usually carried out, did not necessarily give the true value of Young's Modulus, despite the refinements of physical measurement of which modern extensometers are capable. It has been claimed for these instruments that they are capable of measuring down to 10^{-5}, and even 10^{-6}, of an inch. It became a matter of interest, and of some practical importance, to inquire to what extent the method was in itself reliable as a means of determining the particular physical constant. If the claims put forth on behalf of the extensometers were valid, one could measure a movement to within 0·2 per cent. of its true value; but such refinement is futile unless the method can be made at least as reliable as this.

Of the literature on the subject I have made most use of a paper by Prof. L. N. G. Filon †; of papers subsequent thereto I have consulted one by Dr. J. Dougall ‡. The former of these contains a section devoted to historical references, and no further mention thereof will here be made. In those portions of Filon's paper which are relevant to the present discussion, the analysis is limited by the assumption that no movement takes place at the periphery of the end face of the test piece; afterwards a correction is made for the case where there is movement of known amount. In actual practice it would be exceedingly difficult to say precisely what the magnitude of such movement would be; I have therefore so analysed the problem that no such measurement is necessary.

* Communicated by the Director.

† "On the Elastic Equilibrium of Circular Cylinders under Certain Practical Systems of Load," Phil. Trans. Roy. Soc. ser. A, vol. cxcviii. (1902).

‡ "An Analytical Theory of the Equilibrium of an Isotropic Elastic Rod of Circular Section," Trans. Roy. Soc. Edinb. vol. xlix. (1913–14).

The present paper falls into three sections, of which two are quite short. The first section seeks to explain why plane sections do not necessarily remain plane after loading. The second section determines the conditions requisite for a correct evaluation of Young's Modulus and Poisson's Ratio. The third section seeks to give a method of determining Young's Modulus even when the conditions laid down in the second section are violated. Though the applications of the paper are Mechanical rather than Mathematical, the treatment can hardly be described as elementary, and as the third section is somewhat long an indication of its mode of development will be given here.

It can be shown that when the displacements in a body are symmetrical about an axis, the strains and principal stresses can all be expressed in terms of a single function which satisfies a partial differential equation of the fourth order. The number of solutions to this equation is infinite, but two types are chosen :—

(i.) solutions involving circular and Bessel functions,
(ii.) a finite polynomial.

From these a solution is formed by multiplying them by constants and combining them additively. This solution is then made to fit the requisite boundary conditions, thereby establishing certain relations among the constants. By a suitable choice it eventuates that the number of these relations is adequate to the solution of the problem. No cognisance is taken of the actual distribution of the load provided it be symmetrically disposed about the axis. The contraction of a known length and the extension of a diameter of the mid-section are computed ; these can be measured by extensometers, and on these measurements the calculation of Young's Modulus is based. It appears in the sequel that the accurate determination of Young's Modulus is indissolubly bound up with a knowledge of the value of Poisson's Ratio.

Section I.

In applying the Mathematical theory of Elasticity to the study of the behaviour of short cylinders in compression, there are certain obvious advantages in employing the cylindrical polar system of coordinates r, θ, z; where z is measured along the axis of the cylinder, r is measured from this axis, and θ from some axial plane of reference.

During a test, the load will, as far as possible, be applied symmetrically about the axis, and the resulting displacements may be regarded as symmetrical. This gives rise to certain simplifications of the fundamental equations: two of the three "rotations" of the polar element are obviously zero, viz., those about the axis of z and about the horizontal (radial) axis, while differentiations with respect to θ disappear. The equilibrium equations are reduced from three to two in number.

If u, v, w denote displacements in the directions r, θ, z respectively we have $v=0$, and for the strains (in the usual notation)

$$\left.\begin{aligned} e_{rr} &= \frac{\partial u}{\partial r}, \quad e_{zz} = \frac{\partial w}{\partial z}, \quad e_{\theta z} = e_{r\theta} = 0, \\ e_{\theta\theta} &= \frac{u}{r}, \quad\quad e_{rz} = \frac{\partial u}{\partial z} + \frac{\partial w}{\partial r}. \end{aligned}\right\} \quad . \quad . \quad . \quad (1)$$

The dilatation

$$\Delta = \frac{\partial u}{\partial r} + \frac{u}{r} + \frac{\partial w}{\partial z}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and for the "rotations" we have

$$\varpi_r = \varpi_z = 0, \quad 2\varpi_\theta = \frac{\partial u}{\partial z} - \frac{\partial w}{\partial r}. \quad . \quad . \quad . \quad . \quad (3)$$

Certain experiments have been carried out on prisms of gelatinous material with coloured threads inserted. It was found that the threads, being originally horizontal, became curved as the prism was compressed. The explanation is as follows:—Working in cylindrical polar coordinates, without necessarily confining ourselves to symmetrical displacements, the assumption that horizontal plane sections remain plane and horizontal after loading is expressed analytically by the equations

$$\frac{\partial w}{\partial r} = 0 = \varpi_\theta.$$

From equation (3), which gives the form of ϖ_θ, we have immediately $\dfrac{\partial u}{\partial z} = 0$, which shows that the radial displacement is independent of z and must be the same at all levels, including the end faces. The curving of the threads indicates that the free motion of the end faces was impeded.

Section II.

For the stresses we have

$$\left.\begin{aligned} \widehat{rr} &= \lambda\Delta + 2\mu\frac{\partial u}{\partial r}, \quad \widehat{\theta z} = \widehat{\theta r} = 0, \\ \widehat{\theta\theta} &= \lambda\Delta + 2\mu\frac{u}{r}, \quad \widehat{zr} = \mu\left(\frac{\partial u}{\partial z} + \frac{\partial w}{\partial r}\right), \\ \widehat{zz} &= \lambda\Delta + 2\mu\frac{\partial w}{\partial z}. \end{aligned}\right\} \quad . \quad (4)$$

Since we are concerned only with equilibrium conditions, and as there are no body forces in operation, the equilibrium equations are :

$$\left.\begin{aligned} \frac{\partial}{\partial r}(\widehat{rr}) + \frac{\partial}{\partial z}(\widehat{rz}) + \frac{\widehat{rr} - \widehat{\theta\theta}}{r} &= 0, \\ \frac{\partial}{\partial r}(\widehat{rz}) + \frac{\partial}{\partial z}(\widehat{zz}) + \frac{\widehat{rz}}{r} &= 0, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (5)$$

which can be written as

$$\left.\begin{aligned} (\lambda + 2\mu)\frac{\partial\Delta}{\partial r} + 2\mu\frac{\partial\varpi_\theta}{\partial z} &= 0, \\ (\lambda + 2\mu)\frac{\partial\Delta}{\partial z} - 2\frac{\mu}{r}\frac{\partial}{\partial r}(r\varpi_\theta) &= 0. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (6)$$

Suppose that the deformations are linear, i.e. u, w are linear functions of r, z ; so that we write

$$u = \alpha z + \beta r, \quad w = \alpha' z + \beta' r,$$

whence $\Delta = \alpha' + 2\beta + \alpha z/r.$

Then

$$2\varpi_\theta = \frac{\partial u}{\partial z} - \frac{\partial w}{\partial r} = \alpha - \beta', \text{ and } \frac{\partial\varpi}{\partial z} = 0.$$

The former of equations (6) then shows that $\dfrac{\partial\Delta}{\partial r} = 0$, *i.e.* Δ is independent of r, whence $\alpha = 0$, leaving $\Delta = 2\beta + \alpha'$, whence $\dfrac{\partial\Delta}{\partial z} = 0$ and $2\varpi_\theta = -\beta'$. The latter of equations (6) now shows that $\dfrac{\partial}{\partial r}(r\varpi_\theta) = 0$, so that $\beta' = 0$. Consequently

$$u = \beta r, \quad w = \alpha' z, \quad \Delta = 2\beta + \alpha'.$$

From equations (4) we have

$$\begin{aligned}\widehat{rr} &= \lambda\Delta + 2\mu\frac{\partial u}{\partial r}\\ &= \lambda(2\beta+\alpha') + 2\mu\beta\\ &= \lambda\alpha' + 2\beta(\lambda+\mu).\end{aligned}$$

If no force is applied to the curved surface, $\widehat{rr}=0$ at the boundary and we deduce

$$\frac{\lambda}{2(\lambda+\mu)} = -\frac{\beta}{\alpha'}.$$

Similarly

$$\begin{aligned}\widehat{zz} &= \lambda\Delta + 2\mu\frac{\partial w}{\partial z}\\ &= \lambda(2\beta+\alpha') + 2\mu\alpha'\\ &= \alpha'(\lambda+2\mu) + 2\beta\lambda = -\mathrm{P}, \text{ say},\end{aligned}$$

which means that the end pressure is uniform and normal to the face inwards. We deduce

$$\left.\begin{aligned}\alpha' &= -\frac{\mathrm{P}(\lambda+\mu)}{\mu(3\lambda+2\mu)} = -\frac{\mathrm{P}}{\mathrm{E}},\\ \beta &= \frac{\mathrm{P}\lambda}{2\mu(3\lambda+2\mu)} = \frac{\mathrm{P}\sigma}{\mathrm{E}},\end{aligned}\right\}$$

where E = Young's Modulus,
σ = Poisson's Ratio.

The conclusion is that Young's Modulus is correctly given by (stress/strain), as is Poisson's Ratio by (lateral expansion/longitudinal contraction), provided $\widehat{zz}$ is uniform and $\widehat{rr}$ is independent of z. These two provisos mean that the end pressure must be uniformly distributed, and all horizontal cross-sections (including the end faces) must expand equally. The conditions are invalidated by any form of end constraint. The insertion of cardboard, for example, between the face-plate and the specimen would introduce a frictional restraint if the cardboard failed to flow as readily as the specimen. On the other hand, sheet lead similarly inserted would have the opposite effect if it flowed more readily than did the specimen, thereby tending to compel the test piece to move overmuch. The tendency of an end constraint, either by friction or imbedding in the face plate, is to curve the plane end of the test piece, thereby destroying the uniformity of pressure distribution and creating high local stresses.

Section III.

Since it is impossible to guarantee the complete absence of end restraints in a compression test, and since the presence of such restraints invalidates the experiment as a means of finding Young's Modulus, it remains to find what useful information can be derived from a compression test.

From a survey of equations (2), (3), and (6) it seems apparent that all the quantities (except the fundamental variables r, θ, z) should be expressible in terms of a single function. For theoretically ϖ_θ is determined in terms of Δ from equation (6), and equations (2) and (3) then determine u and w in terms of Δ also. The actual results, which need not be deduced here, are given elsewhere *. They are:

$$\left.\begin{aligned}
\widehat{rr} &= \frac{\partial}{\partial z}\left\{\sigma\nabla^2\chi - \frac{\partial^2\chi}{\partial r^2}\right\}, & \widehat{rz} &= \frac{\partial}{\partial r}\left\{(1-\sigma)\nabla^2\chi - \frac{\partial^2\chi}{\partial z^2}\right\},\\
\widehat{\theta\theta} &= \frac{\partial}{\partial z}\left\{\sigma\nabla^2\chi - \frac{1}{r}\cdot\frac{\partial\chi}{\partial r}\right\}, & u &= -\frac{1+\sigma}{\mathrm{E}}\cdot\frac{\partial^2\chi}{\partial r\,.\,\partial z},\\
\widehat{zz} &= \frac{\partial}{\partial z}\left\{(2-\sigma)\nabla^2\chi - \frac{\partial^2\chi}{\partial z^2}\right\}, & w &= \frac{1+\sigma}{\mathrm{E}}\left\{(1-2\sigma)\nabla^2\chi + \frac{\partial^2\chi}{\partial r^2} + \frac{1}{r}\cdot\frac{\partial\chi}{\partial r}\right\}\\
& & &= \frac{1+\sigma}{\mathrm{E}}\left\{2(1-\sigma)\nabla^2\chi - \frac{\partial^2\chi}{\partial z^2}\right\},
\end{aligned}\right\} \quad (7)$$

where σ = Poisson's Ratio, E = Young's Modulus, and ∇^2 denotes Laplace's operator $\dfrac{\partial^2}{\partial x^2}+\dfrac{\partial^2}{\partial y^2}+\dfrac{\partial^2}{\partial z^2}$, and χ satisfies the equation $\nabla^4\chi = 0$. With regard to the operator ∇^2, we note that in cylindrical coordinates it takes the form

$$\frac{1}{r}\cdot\frac{\partial}{\partial r}\left(r\cdot\frac{\partial}{\partial r}\right)+\frac{1}{r^2}\cdot\frac{\partial^2}{\partial\theta^2}+\frac{\partial^2}{\partial z^2},$$

and as we are at present concerned only with symmetrical displacements, the middle term of these three disappears. The operator therefore reduces to

$$\frac{1}{r}\cdot\frac{\partial}{\partial r}\left(r\cdot\frac{\partial}{\partial r}\right)+\frac{\partial^2}{\partial z^2} = \frac{\partial^2}{\partial r^2}+\frac{1}{r}\cdot\frac{\partial}{\partial r}+\frac{\partial^2}{\partial z^2}.$$

To determine suitable forms for χ we note that every solution of $\nabla^2\chi = 0$ is necessarily a solution of $\nabla^4\chi = 0$. The first step, therefore, is to determine suitable solutions of $\nabla^2\chi = 0$. Accordingly we assume as a possible solution,

$$\chi = f(r)\,.\,\phi(z).$$

* Love, 'Mathematical Theory of Elasticity,' 3rd edit. p. 278.

The equation $\nabla^2\chi=0$ then becomes

$$\frac{1}{r}\cdot\phi\,.\,f'+\phi\,.\,f''+f\,.\,\phi''=0,$$

or

$$\frac{f''+\frac{1}{r}f'}{f}+\frac{\phi''}{\phi}=0,$$

where primes denote differentiations. As the former term contains only r and the latter only z, we conclude that each is a constant, *i. e.*,

$$\frac{\phi''}{\phi}=k^2, \quad \text{or} \quad \phi''-k^2\phi=0,$$

and

$$\frac{f''+\frac{1}{r}f'}{f}=-k^2, \text{ or } f''+\frac{1}{r}f'+k^2f=0.$$

The former of these yields $\phi=e^{\pm kz}$, and the latter, on substituting $t=kr$, gives the Bessel equation of order zero. Its solution is therefore $f=\mathrm{J}_0(kr)$, and the complete solution is

$$\chi=e^{\pm kz}\,.\,\mathrm{J}_0(kr),$$

where k is any constant.

Forms of χ which satisfy $\nabla^4\chi=0$ but not $\nabla^2\chi=0$ can be found as follows. If χ contains a parameter k, we have

$$\frac{\partial}{\partial k}\nabla^4\chi=\nabla^4\frac{\partial\chi}{\partial k}=0,$$

which shows that $\dfrac{\partial\chi}{\partial k}$ is a solution. Now

$$\frac{\partial}{\partial k}\{e^{kz}\,.\,\mathrm{J}_0(kr)\}=z\,.\,e^{kz}\,\mathrm{J}_0(kr)+e^{kz}\,.\,\frac{\partial\mathrm{J}_0(kr)}{\partial r}\,.\,\frac{\partial r}{\partial(kr)}\,.\,\frac{\partial(kr)}{\partial k}$$

$$=z\,.\,e^{kz}\,\mathrm{J}_0(kr)+\frac{r}{k}\,.\,e^{kz}\,.\,\frac{\partial}{\partial r}\mathrm{J}_0(kr).\quad .\quad .\quad (8)$$

Also

$$\nabla^2\left\{r\,.\,e^{kz}\,\frac{\partial}{\partial r}\mathrm{J}_0(kr)\right\}=-2k^2\,.\,e^{kz}\,.\,\mathrm{J}_0(kr),$$

which proves that each term on the right of equation (8) is separately a solution of $\nabla^4\chi=0$. [Examination shows the former of these two to be of little value in the present investigation ; we therefore confine ourselves to the latter of the two.]

Hitherto no restrictions have been placed on the constant k, which may be real or imaginary. If we take it as imaginary,

and remember that $J_0(x)=J_0(-x)$, we can add or subtract corresponding pairs of solutions, thus deducing solutions of the types

$$\begin{matrix}\sin\\ \cos\end{matrix}(kz)\,.\,I_0(kr), \quad r\begin{matrix}\sin\\ \cos\end{matrix}(kz)\frac{\partial}{\partial r}I_0(kr),$$

where I_0 is the modified Bessel function of the first kind. The modified Bessel functions of the second kind, the so-called K functions, are useless for our present purpose owing to their infinities on the axis. If we take the origin of coordinates at the middle of the axis of the cylinder, we see from equations (7) that χ must be an odd function of z and an even function of r. We therefore reject the cosine terms and retain only solutions of the types

$$\chi_1 = \sin(kz)\,.\,I_0(kr),$$

$$\chi_2 = r\,.\,\sin(kz)\,.\frac{\partial}{\partial r}I_0(kr) = r\,.\,\sin(kz)\,.\,I'_0(kr).$$

In addition to the foregoing periodic solutions we can find a finite polynomial solution. To be odd in z and even in r, it must have the form

$$\begin{aligned}\chi_3 = \quad & a_1 z \\ & + a_3 z^3 + b_1 r^2 z \\ & + a_5 z^5 + b_3 r^2 z^3 + c_1 r^4 z \\ & + a_7 z^7 + b_5 r^2 z^5 + c_3 r^4 z^3 + d_1 r^6 z \\ & + \ldots . \\ & + \ldots . .\end{aligned}$$

As this has to satisfy $\nabla^4\chi_3=0$, there will be certain relations between these coefficients. The operator ∇^4, written at length, is

$$\delta^4+\frac{2}{r}\delta^3-\frac{1}{r^2}\delta^2+\frac{1}{r^3}\delta+2\delta^2\mathrm{D}^2+\frac{2}{r}\delta\mathrm{D}^2+\mathrm{D}^4,$$

where

$$\delta=\frac{\partial}{\partial r}, \quad \mathrm{D}=\frac{\partial}{\partial z},$$

and on evaluating $\nabla^4\chi_3$ it will be found that

(i.) terms of degree 1 and 3 satisfy identically,

(ii.) terms of degree 5 require

$$15a_5+6b_3+8c_1=0, \quad . \quad . \quad . \quad (9)$$

(iii.) terms of degree 7 require

$$105a_7+20b_5+8c_3=0, \quad . \quad . \quad . \quad (10)$$

and

$$5b_5+8c_3+24d_1=0, \quad . \quad . \quad . \quad (11)$$

and so on. This can be continued to any desired degree.

As χ_1, χ_2, and χ_3 are all solutions of $\nabla^4\chi=0$, it follows that $A\chi_1+B\chi_2+\chi_3$ is also a solution, where A, B are any constants. The general solution can be written

$$\sum_{n=1}^{\infty}\{A_n \sin(k_nz)I_0(k_nr)+B_nr\sin(k_nz)I_0'(k_nr)\}+\chi_3.$$

It remains to choose the A's, B's, and k's to satisfy given boundary conditions. To do this, it is an advantage to know the quota from χ_1, χ_2 to each of the quantities in equations (7). We find these, using primes to denote differentiations with respect to r and taking advantage of the relation

$$I_0''(kr)+\frac{1}{r}.I_0'(kr)=k^2I_0(kr).$$

We further abbreviate by omitting all arguments—which for the Bessel functions are (kr), and for the trigonometrical functions are (kz)—and write S for $\sin(kz)$, C for $\cos(kz)$. The results, which can be easily verified, are tabulated here :—

	From χ_1	From χ_2
$\widehat{rr}$	$-kCI_0''$	$k^3C\{(2\sigma-1)I_0-rI_0'\}$
to $\widehat{\theta\theta}$	$-kCI_0'/r$	$k^3(2\sigma-1)CI_0$
to $\widehat{zz}$	k^3CI_0	$k^3C\{2(2-\sigma)I_0+rI_0'\}$
to $\widehat{rz}$	k^2SI_0'	$k^2S\{k^2rI_0+2(1-\sigma)I_0'\}$
to u	$-\frac{1+\sigma}{E}kCI_0'$	$-\frac{1+\sigma}{E}k^3rCI_0$
to w	$\frac{1+\sigma}{E}k^2SI_0$	$\frac{1+\sigma}{E}.k^2S\{4(1-\sigma)I_0+rI_0'\}$

Probably the most likely condition to be attained in practice is that of keeping the ends of the test piece flat, especially if the face plates were very hard. We will proceed on this assumption. Analytically this will mean that w is independent of r when $z=h$, where $2h=$height of cylinder. The above table shows that w can be made independent of r provided (i.) $\sin(kh)=0$, (ii.) χ_3's quota to w is independent of r. The former proviso fixes the k's, giving $kh=n\pi$, where n is an integer. The second proviso needs some examination.

If we use equations (7) to evaluate χ_3's quota to $\frac{Ew}{1+\sigma}$,

we get, on the assumption that χ_3 stops at terms of degree 7, an expression of the form

$$L+Mr^2+Nr^4,$$

where L, M, and N are functions of z. To carry out the second of the aforementioned provisos we therefore require $N=M=0$ when $z=h$. The work of evaluating M and N from the expression for χ_3 yields

$$(1-2\sigma)c_3+12(1-\sigma)d_1=0 \quad . \quad . \quad . \quad . \quad (12)$$

and

$$(1-2\sigma)(3b_3+10b_5h^2)+16(1-\sigma)(c_1+c_3h^2)=0. \quad (13)$$

We now make $\widehat{rz}$ vanish over the curved surface, *i. e.* when $r=a$, where "a" is the radius of the test piece. A glance at the tabulated results shows that the quota from χ_1, χ_2 to $\widehat{rz}$ vanish identically when $z=h$, since $\sin(kh)\equiv 0$. It follows that χ_3's quota to $\widehat{rz}$ must vanish in similar circumstances, *i. e.*, when $r=a$ and $z=h$. The actual evaluation of χ_3's quota to $\widehat{rz}$ yields as an equation of condition,

$$(1-\sigma)(8c_1+8c_3h^2+36a^2d_1)=\sigma(3b_3+6c_3a^2+10b_5h^2). \quad (14)$$

The last six equations (9) to (14) inclusive enable us to express the six variables a_7, a_5, b_5, b_3, c_3, and c_1 in terms of d_1. On solving them we get

$$a_7=-\frac{32}{35}d_1\frac{2-\sigma}{1-2\sigma}, \quad a_5=\frac{-4d_1}{5(1-2\sigma)}\{8h^2(\sigma-2)+3a^2(3-2\sigma)\},$$

$$b_5=\frac{24}{5}.d_1.\frac{3-2\sigma}{1-2\sigma}, \quad b_3=\frac{8d_1}{(1-2\sigma)}\{2h^2(2\sigma-3)+3a^2(1-\sigma)\},$$

$$c_3=-12d_1.\frac{1-\sigma}{1-2\sigma} \quad c_1=\frac{3d_1}{2(1-2\sigma)}\{8h^2(1-\sigma)-3a^2(1-2\sigma)\}.$$

As χ_3's quota to $\widehat{rz}$ is found to be actually

$$4rz[(1-\sigma)(8c_1+8c_3z^2+36r^2d_1)-\sigma(6c_3r^2+3b_3+10b_5z^2)],$$

it reduces at the curved surface $r=a$ to

$$192ad_1z(h^2-z^2)(2-\sigma)/(1-2\sigma).$$

In this the z and z^3 can be replaced by series of sines of multiples of $(\pi z/h)$ by the relations

$$z=\sum_1^\infty(-1)^{n-1}\frac{2h}{n\pi}\sin\frac{n\pi z}{h},$$

$$z^3=\sum_1^\infty(-1)^{n-1}\left(\frac{2h^3}{n\pi}-\frac{12h^3}{n^3\pi^3}\right)\sin\frac{n\pi z}{h}.$$

The value of $\widehat{rz}$, as determined from the general solution given at the top of p. 471, can now be expressed as a series of sines of multiples of $(\pi z/h)$. Consequently $\widehat{rz}$ vanishes over the curved surface if the coefficient of each sine vanishes separately. As coefficient of $\sin(n\pi z/h)$ we have

$$A_n k_n^2 I_0'(k_n a) + B_n k_n^2 \{k_n^2 a I_0(k_n a) + 2(1-\sigma) I_0'(k_n a)\} + 192 a d_1 \frac{(2-\sigma)}{(1-2\sigma)} \frac{12h^3}{n^3\pi^3}(-1)^{n-1} = 0, \quad (15)$$

which gives one relation between A_n and B_n.

We now make $\widehat{rr}$ vanish over the curved surface. The quota from χ_3 to $\widehat{rr}$, when evaluated for $r=a$, is of the form $L + Mz^2 + Nz^4$, where

$$L = 2b_1(2\sigma-1) + 6\sigma a_3 + \frac{12 a d_1}{(1-2\sigma)}\{a^2(2-\sigma) - 4h^2(3-\sigma)\},$$

$$M = \frac{144 d_1}{(1-2\sigma)}\{a^2(2-\sigma) + 2h^2\}, \quad N = -\frac{144 d_1}{(1-2\sigma)}.$$

For the z and z^4 terms we can substitute series of cosines from the relations

$$z^2 = \frac{h^2}{3} + \sum_{n=1}^{\infty}\left(\frac{2h}{n\pi}\right)^2 (-1)^n \cos\frac{n\pi z}{h},$$

$$z^4 = \frac{h^4}{5} + \sum_{n=1}^{\infty} 8h^4(-1)^n\left(\frac{1}{n^2\pi^2} - \frac{6}{n^4\pi^4}\right)\cos\frac{n\pi z}{h}.$$

The value of $\widehat{rr}$ (at $r=a$) as determined from the general solution on p. 471 can be expressed as an independent term plus a series of cosines of multiples of $(\pi z/h)$; for χ_1 and χ_2 contribute cosines, *vide* table on p. 471. Consequently we can make $\widehat{rr}$ vanish over the curved surface if we equate the independent term and the coefficient of each cosine separately to zero. The latter gives

$$-A_n \cdot \frac{n\pi}{h} I_0''\left(\frac{n\pi a}{h}\right) + B_n\left(\frac{n\pi}{h}\right)^3 \left\{(2\sigma-1) I_0\left(\frac{n\pi a}{h}\right) - a I_0'\left(\frac{n\pi a}{h}\right)\right\} + \frac{144}{(1-2\sigma)} \cdot \frac{4h^2 d}{n^2\pi^2} \cdot (-1)^n \left\{\frac{12h}{n^2\pi^2} + a^2(2-\sigma)\right\} = 0, \quad (16)$$

which, with equation (15) *supra*, serves to determine the A's

and B's. The independent term gives

$$L + \tfrac{1}{3}Mh^2 + \tfrac{1}{5}Nh^4 = 0,$$

or

$$b_1(1-2\sigma) - 3a_3\sigma = \frac{6d_1}{(1-2\sigma)}\{a^4(2-\sigma) - 4a^2h^2 + \tfrac{28}{5}h^4\}. \quad . \quad . \quad . \quad (17)$$

We now have to make the total end load equal to a given quantity, *i.e.*,

$$-\pi a^2 Q = \iint \widehat{zz} \,.\, r \,.\, d\theta \,.\, dr,$$

or

$$-\frac{a^2 Q}{2} = \int_0^a \widehat{zz} \,.\, r \,.\, dr,$$

where Q=average load per unit area. In order to effect this integration it is convenient to take $\widehat{zz}$ in parts. The quota to $\widehat{zz}$ from χ_3 becomes, when $z=h$,

$$4b_1(2-\sigma) + 6a_3(1-\sigma) + \frac{12d_1}{(1-2\sigma)}\{12a^2h^2(1-\sigma) - 8h^4(2-\sigma) + 6a^2r^2\sigma - 16h^2r^2(1-\sigma) - 3r^4\sigma\}.$$

If we substitute this in the integral $\int_0^a \widehat{zz} \,.\, r \,.\, dr$ and evaluate, we get

$$a^2\{2b_1(2-\sigma) + 3a_3(1-\sigma)\} + \frac{12a^2d_1}{(1-2\sigma)}\{a^4\sigma + 2a^2h^2(1-\sigma) - 4h^4(2-\sigma)\}.$$

The quota to $\widehat{zz}$ from $A\chi_1 + B\chi_2$ can be written in brief as

$$k^3C[AI_0 + B\{2(2-\sigma)I_0 + rI_0'\}].$$

We substitute this in $\int_0^a z\widehat{z} \,.\, r \,.\, dr$ and evaluate, *i. e.*,

$$k^3C\int_0^a [\{A + 2B(2-\sigma)\}I_0 r + Br^2 I_0'] \,.\, dr.$$

Now

$$\int r^2 I_0' \,.\, dr = r^2 I_0 - 2\int r I_0 \,.\, dr,$$

so that the above integral becomes

$$k^3C\int_0^a \{A + 2B(1-\sigma)\}I_0 \,.\, r \,.\, dr + Bk^3 a\, CI_0(ka).$$

Also, from the relation

$$I_0'' + \frac{1}{r}I_0' = k^2 I_0,$$

we have

$$\int r \,.\, I_0'' \,.\, dr + \int I_0' \,.\, dr = k^2 \int r \,.\, I_0 \,.\, dr\,;$$

whence $$\int_0^a [rI_0'] = k^2 \int_0^a rI_0 \,.\, dr,$$

so that the above integral becomes

$$kaC[AI_0' + B\{2(1-\sigma)I_0' + ak^2 I_0\}].$$

The value of this is given by equation (15).

When $\widehat{zz}$ is determined from the more general value $\sum_{n=1}^{\infty}(A\chi_1 + B\chi_2)$, the integral

$$\int_0^a \widehat{zz} \,.\, r \,.\, dr = 12.192 a^2 d_1 \frac{(2-\sigma)}{(1-2\sigma)} \cdot \frac{h^4}{\pi^4} \sum_1^{\infty} \frac{(-1)^n}{n^4} \cos\frac{(n\pi z)}{h},$$

when $z = h$.

Using

$$\sum_1^{\infty} (-1)^n n^{-4} \,.\, \cos\left(\frac{n\pi z}{h}\right) = -\pi^4 \left\{ \frac{z^4}{48h^4} - \frac{z^2}{24h^2} + \frac{7}{720} \right\}$$

$$= \frac{\pi^4}{90}, \text{ when } z = h,$$

the above reduces to $\frac{128}{5} \,.\, h^4 a^2 d_1 \frac{(2-\sigma)}{(1-2\sigma)}$. The equation for the end pressure, Q, therefore gives ultimately

$$-\frac{Q}{2} = 2b_1(2-\sigma) + 3a_3(1-\sigma) + \frac{12 d_1}{(1-2\sigma)} \left\{ a^4\sigma + 2a^2h^2(1-\sigma) - \frac{28}{15} h^4 (2-\sigma) \right\} \quad . \quad . \quad . \quad . \quad (18)$$

At this stage of the work the position is as follows. There are five unknown quantities, viz. E, σ, a_3, b_1, and d_1; there are only two relations, viz. (17) and (18). The determination of E is inextricably bound up with σ. At least one physical measurement will have to be made, so that there are three courses open to us for the determination of the necessary three further relations. We can make

(i) one measurement and two assumptions,
or (ii) two measurements and one assumption,
or (iii) three measurements.

This last course, though theoretically sound and on general grounds the most preferable, is beset with considerable difficulties, both Mechanical and Mathematical *. If we make the assumption that σ may be treated as a known quantity, we are left with the option of making

(i) one measurement and one further assumption,
or (ii) two measurements.

* It is hoped to explore this avenue in a future paper.

The one further assumption that recommends itself is to suppose there is no movement at the face-plate, *i. e.*, that the periphery of the end face does not move *. This would be difficult, if not impossible, to ensure in practice and we choose the alternative of making two measurements, which would be (i.) the contraction of a measured axial length, and (ii.) the extension of the diameter of the middle cross-section (*i. e.*, the value of u when $z=0$). These two measurements could be made by using longitudinal and lateral extensometers simultaneously.

We proceed to the second of the two measurements, the value of u when $z=0$ and $r=a$. The quota from χ_3 to $-\frac{Eu}{1+\sigma}$ is

$$\frac{\partial^2\chi_3}{\partial r\,.\,\partial z} = 2b_1r + 6b_3rz^2 + 4c_1r^3 + 10b_5rz^4 + 12c_3r^3z^2 + 6d_1r^5.$$

When $r=a$ and $z=0$, this evaluates to

$$2ab_1 - 12a^5d_1 + 48a^3h^2d_1\frac{(1-\sigma)}{(1-2\sigma)} - 48ah^4d_1\frac{(3-2\sigma)}{(1-2\sigma)}.$$

The quota from $A\chi_1 + B\chi_2$ can be determined thus. Its value, from p. 471, is $Ak\mathrm{C}I_0' + Bk^3\mathrm{C}aI_0$. If we put

$$AI_0' + Bk^2aI_0 + \phi = 0, \quad . \quad . \quad . \quad . \quad . \quad (19)$$

where the argument of the Bessel functions is ka, we have from (15), (16), and (19), by eliminating A, B the relation :

$$\begin{vmatrix} I_0', & ak^2I_0 + 2(1-\sigma)I_0', & 4ak^{-2}H(2-\sigma) \\ I_0'', & ak^2I_0' + k^2(1-2\sigma)I_0, & \{12k^{-2} + a^2(2-\sigma)\}H \\ I_0, & k^2aI_0, & \phi \end{vmatrix} = 0,$$

where

$$H = \frac{12.48d_1}{(1-2\sigma)k^3}(-1)^{n-1},$$

whence

$$\frac{\phi}{H} = 4ak^{-2}(2-\sigma) + 2(1-\sigma)\frac{I_0'[I_0'\{a^2(2-\sigma) + 4k^{-2}(5-\sigma)\} - 4a(2-\sigma)I_0]}{ak^4I_0^2 - I_0'^2\{ak^2 + 2(1-\sigma)a^{-1}\}}.$$

The quota from the more general value $\Sigma(A\chi_1 + B\chi_2)$ is therefore $-\Sigma k\phi\cos(n\pi z/h)$, which falls into two parts

* This is the assumption made in Filon's paper, *l. c.*

from the known value of ϕ above. The first part gives $-\Sigma 4ak^{-1}\mathrm{H}(2-\sigma)\cos \pi z/h$, which, when $z=0$, reduces to $-\frac{112}{5}ah^4d_1\frac{(2-\sigma)}{(1-2\sigma)}$. The second part gives

$$+24.48ad_1\frac{(1-\sigma)}{(1-2\sigma)}\Sigma\frac{\mathrm{I}_0'[\mathrm{I}_0'\{a^2(2-\sigma)+4k^{-2}(5-\sigma)\}-4a(2-\sigma)\mathrm{I}_0]}{k^2[a^2k^4\mathrm{I}_0^2-\mathrm{I}_0'^2\{a^2k^2+2(1-\sigma)\}]}(-1)^n.$$

Since

$$\mathrm{I}_0'(kr)=\frac{\partial}{\partial r}\mathrm{I}_0(kr)=k\mathrm{I}_1(kr),$$

we deduce that the value of u when $z=0$, $r=a$ is

$$-\frac{1+\sigma}{\mathrm{E}}\Big[2ab_1-12a^5d_1+48a^3h^2d_1\frac{(1-\sigma)}{(1-2\sigma)}-\frac{16}{5}ah^4d_1\frac{(59-37\sigma)}{(1-2\sigma)}$$
$$+24.48ad_1\frac{(1-\sigma)}{(1-2\sigma)}\Sigma\frac{\mathrm{I}_1^2\{a^2k^2(2-\sigma)+4(5-\sigma)\}-4ak(2-\sigma)\mathrm{I}_0\mathrm{I}_1}{k^4[a^2k^2(\mathrm{I}_0^2-\mathrm{I}_1^2)-2\mathrm{I}_1^2(1-\sigma)]}(-1)^n\Big]. \quad . \quad . \quad . \quad (20)$$

In a similar manner we now determine the former of the two measurements, *i. e.*, the contraction of an axial length, l, say. The quota from χ_3 to w is given by

$$\frac{\mathrm{E}w}{(1+\sigma)}=8b_1z(1-\sigma)+6a_3z(1-2\sigma)+20a_5z^3(1-2\sigma)$$
$$+8b_3z^3(1-\sigma)+8b_5z^5(1-\sigma)+42a_7z^5(1-2\sigma)$$
$$+r^2[32c_1z(1-\sigma)+6b_3z(1-2\sigma)+32c_3z^3(1-\sigma)$$
$$+20b_5z^3(1-2\sigma)]$$
$$+r^4[72d_1z(1-\sigma)+6c_3z(1-2\sigma)].$$

If we compute this for $r=a$, $z=l$, it yields

$$2l\{4b_1(1-\sigma)+3a_3(1-2\sigma)\}$$
$$-\frac{48a^2d_1l^3}{1-2\sigma}-\frac{128d_1h^2l^3}{1-2\sigma}+\frac{96a^2h^2d_1l}{1-2\sigma}+\frac{192d_1l^5}{5(1-2\sigma)}.$$

The quota to $\mathrm{E}w/(1+\sigma)$ from $\mathrm{A}\chi_1+\mathrm{B}\chi_2$ is

$$k^2\mathrm{S}[\mathrm{AI}_0+\mathrm{B}\{4(1-\sigma)\mathrm{I}_0+a\mathrm{I}_0'\}].$$

Put

$$\mathrm{AI}_0+\mathrm{B}\{4(1-\sigma)\mathrm{I}_0+a\mathrm{I}_0'\}+\theta=0,$$

so that, as for the determination of ϕ, we get

$$\begin{vmatrix} \mathrm{I}_0', & ak^2\mathrm{I}_0+2(1-\sigma)\mathrm{I}_0', & 4ak^{-2}\mathrm{H}(2-\sigma) \\ \mathrm{I}_0'', & ak^2\mathrm{I}_0'-k^2(2\sigma-1)\mathrm{I}_0, & \{12k^{-2}+a^2(2-\sigma)\}\mathrm{H} \\ \mathrm{I}_0, & 4(1-\sigma)\mathrm{I}_0+a\mathrm{I}_0', & \theta \end{vmatrix}=0,$$

whence

$$\frac{\theta}{H} = k^{-4}\{4(2\sigma^2-7\sigma+9)+a^2k^2(2-\sigma)\}$$

$$-(1-\sigma)I_0'.\frac{I_0\{8(7-2\sigma)k^{-2}+2a^2(2-\sigma)\}-I_0'\{10a(2-\sigma)k^{-2}+8(2\sigma^2-7\sigma+9)a^{-1}k^{-4}\}}{ak^4I_0^2-I_0'^2\{ak^2+2(1-\sigma)a^{-1}\}}.$$

The quota from the more general value $\Sigma(A\chi_1+B\chi_2)$ is therefore $-\Sigma k^2\theta\sin(kl)$, which falls into two parts from the known value of θ above. The first part gives

$$12.48d_1(1-2\sigma)^{-1}[4(2\sigma^2-7\sigma+9)k^{-5}+a^2(2-\sigma)k^{-3}](-1)^n\sin(kl).$$

As

$$\sum\frac{(-1)^n}{k^3}\sin(kl)=\left(\frac{h}{\pi}\right)^3\sum\frac{(-1)^n}{n^3}\sin\left(\frac{n\pi l}{h}\right)=\frac{l(l^2-h^2)}{12}$$

and

$$\sum\frac{(-1)^n}{k^5}\sin(kl)=\left(\frac{h}{\pi}\right)^5\sum\frac{(-1)^n}{n^5}\sin\left(\frac{n\pi l}{h}\right)$$
$$=-\frac{l}{24}\left(\frac{7h^4}{30}-\frac{h^2l^2}{3}+\frac{l^4}{10}\right),$$

this first part would give

$$-\frac{12.48d_1l}{(1-2\sigma)}\left[\frac{(2\sigma^2-7\sigma+9)}{6}\left(\frac{7h^4}{30}-\frac{h^2l^2}{3}+\frac{l^4}{10}\right)+\frac{a^2(2-\sigma)(h^2-l^2)}{12}\right].$$

It may be shown, too, that the second part would give on reduction:

$$12.48ad_1\frac{(1-\sigma)}{(1-2\sigma)}\sum\frac{I_0I_1\{8(7-2\sigma)+2a^2k^2(2-\sigma)\}-I_1^2\{10ak(2-\sigma)+8(2\sigma^2-7\sigma+9)/ak\}}{k^4\{a^2k^2(I_0^2-I_1^2)-2(1-\sigma)I_1^2\}}\times(-1)^{n-1}\sin(kl)$$

$$=Md_1, \text{ say.}$$

The actual value of $\frac{Ew}{(1+\sigma)}$ is therefore

$$2l\{4b_1(1-\sigma)+3a_3(1-2\sigma)\}$$
$$+Md_1+\frac{16d_1l}{(1-2\sigma)}\left[3a^2h^2\sigma+3(1-\sigma)a^2l^2+2(1-\sigma)(5-2\sigma)h^2l^2-\frac{7h^4}{5}(2\sigma^2-7\sigma+9)-\frac{3l^4}{5}(2\sigma^2-7\sigma-11)\right]. \quad (21)$$

We are now in possession of the necessary four relations, viz. (17), (18), (20), and (21), and since the quantities

(h/a), (l/a) are purely numerical, as is ak, we may re-write these relations in the forms :

$$b_1(1-2\sigma) - \quad 3a_3\sigma \quad - \mathrm{A}a^4d_1(1-2\sigma)^{-1} = 0, \quad . \quad . \quad (17a)$$

$$2b_1(2-\sigma) + 3a_3(1-\sigma) - \mathrm{B}a^4d_1(1-2\sigma)^{-1} + \mathrm{Q}/2 = 0, \quad . \quad . \quad (18a)$$

$$2b_1 \qquad - \mathrm{C}a^4d_1(1-2\sigma)^{-1} + \mathrm{E}u/(1+\sigma)a = 0, \quad . \quad . \quad (20a)$$

$$8b_1(1-\sigma) + 6a_3(1-2\sigma) - \mathrm{D}a^4d_1(1-2\sigma)^{-1} + \mathrm{E}w/(1+\sigma)l = 0, \quad . \quad . \quad (21a)$$

where A, B, C, and D are somewhat complicated but purely numerical coefficients. These permit of the elimination of a_3, b_1, and $a^4d_1/(1-2\sigma)$.

When the eliminant is written down in determinant form, the elements of the last column are

$$0, \quad \frac{\mathrm{Q}}{2}, \quad \frac{\mathrm{E}u}{a(1+\sigma)}, \quad \text{and} \quad \frac{\mathrm{E}w}{l(1+\sigma)}.$$

If each of these be divided by the last named, they become

$$0, \quad \frac{(1+\sigma)}{2}\cdot\frac{\mathrm{Q}l}{\mathrm{E}w}, \quad \frac{lu}{aw}, \quad \text{and} \quad 1.$$

Now $\mathrm{Q}l/w$ is the value of E as determined by the experiment ; let us denote it by E′. Further, (lu/aw) is the value of σ as determined by experiment; let us denote it by σ'. The element of the last column can now be written

$$0, \quad \frac{(1+\sigma)}{2}\cdot\frac{\mathrm{E}'}{\mathrm{E}}, \quad \sigma', \quad \text{and} \quad 1.$$

The eliminant is therefore

$$\begin{vmatrix} (1-2\sigma), & -3\sigma, & \mathrm{A}, & 0 \\ 4-2\sigma, & 3-3\sigma, & \mathrm{B}, & \frac{1+\sigma}{2}\cdot\frac{\mathrm{E}'}{\mathrm{E}} \\ 2, & 0, & \mathrm{C}, & \sigma' \\ 8(1-\sigma), & 6(1-2\sigma), & \mathrm{D}, & 1 \end{vmatrix} = 0,$$

which can be written in various forms, of which the neatest is probably

$$\left(\frac{\mathrm{E}'}{\mathrm{E}}-1\right)\{2\mathrm{A}(1-2\sigma)+\mathrm{D}\sigma-\mathrm{C}\} = (\sigma'-\sigma)\left\{\mathrm{D}-2\cdot\frac{2\mathrm{A}\sigma+\mathrm{B}}{(1+\sigma)}\right\}. \quad (22)$$

This relation has some intriguing and even arresting consequences. We notice that, of the two relations $E = E'$, $\sigma = \sigma'$, each is a necessary consequence of the other, which means that the simultaneous experimental determination of Young's Modulus and Poisson's Ratio gives results which are either both correct or both incorrect. Each of the quantities E', σ' is variable with Q but they are connected by a linear relation, so that if various experimental values are determined for different values of Q the plotted results should lie on a straight line. This straight line does not, in general, pass through the origin, though it does pass through the point (E, σ). Slight and erratic departures from collinearity in the plotted observations would be attributable to experimental errors, but systematic variations would indicate that the material under test was æolotropic.

The quantities on which observations would be made are Q, u, and w. The equations (17a) to (21a) show that these three are connected by a linear relation; but there is no definitive relation between any two of these independent of the third, though in a general way they will all increase together. There is no simple connexion between Q and w, and the stress-strain relation of an isotropic material, when exhibited graphically, may quite well show erratic departures from the straight line. Such departures would naturally be attributed to errors of observation: in reality, they may be nothing of the sort. In the same way, a stress-strain relation that is slightly curved instead of being perfectly straight is no guarantee that the material does not obey Hooke's law.

The fact that, observational errors apart, the quantities E', σ' for an isotropic material are connected by a linear relation indicates a method of determining E, σ more accurately if ever the need for such determination arises. The orientation of the line depends on the constants A, B, C, D, and therefore on a, h, and l, *i. e.* on the dimensions of the test piece and the length whose contraction is measured. Two sets of observations carried out without maintaining the ratios $a : h : l$ would suffice. Alternatively, if a torsion test were considered reliable, a second linear relation is given by the connexion $E = 2\mu(1+\sigma)$.

It is of interest to examine the reliability of the ordinary method of determining Young's Modulus. Filon has shown* that, *ceteris paribus*, there is less error to be expected from long specimens than from short ones. He has computed that, for a material of uniconstant isotropy, a very short

* *Loc. cit.*

specimen gives an error that approaches 20 per cent., on the assumption that there is no movement of the periphery of the end face. In the present paper we have abandoned this assumption, so that it is not possible to present exactly analogous figures ; but other illustrative results are given below.

There appears to be no standard practice in the matter of compression tests, but in certain cases it is held to be good practice to have the test piece half as long again as the diameter, and to measure over a length equal to the diameter, i. e., $a=l=2h/3$.

In order to facilitate the computation of the l-functions, I have slightly modified these dimensions by taking $a=l=2h/\pi$. The values of A, B, etc. vary with σ as shown in the table :—

σ.	A.	B.	C.	D.
0·2	156·142	195·697	975·561	269·701
0·25.....	155·842	191·239	940·310	270·806
0·3	155·542	186·780	905·115	271·722
0·35.....	155·242	182·324	869·994	272·518
0·4	154·942	177·870	834·919	273·277

The corresponding forms of equation (22) are :

$$\left(\frac{E'}{E}-1\right)=(\sigma'-\sigma)\times 0{\cdot}2066 \quad \text{when} \quad \sigma = 0{\cdot}2$$
$$0{\cdot}2170 \qquad\qquad 0{\cdot}25$$
$$0{\cdot}2275 \qquad\qquad 0{\cdot}3$$
$$0{\cdot}2344 \qquad\qquad 0{\cdot}35$$
$$0{\cdot}2379 \qquad\qquad 0{\cdot}4$$

It follows that, in general, the percentage error in the determination of E is about 20 per cent. of the actual error in the determination of σ, so that it may easily nullify the refinements of the compressometer. The experimental conditions under which the foregoing analysis is valid are probably best achieved by the three-piece method due to Prof. Coker *.

In conclusion, the arithmetical work contained herein has been done several times *de novo* and I have every hope that it is correct, at least to the number of places given.

* Journal of the Franklin Institute, vol. 196 No. 4, p. 447 (Oct. 1923).

XXXVIII. *On Gas Flow and Pressure Changes in Gases under Electric Discharge.* *By* R. G. Lunnon, *M.A., M.Sc., Armstrong College, Newcastle-upon-Tyne* *.

THE experiments here recorded were made to measure the viscosity of gases whilst an electric discharge is passing through them. On the theoretical side the problem is a very complicated one, but it appears to merit examination, because of the possibility that, while the excited atoms are radiating energy, their electron orbits may be enlarged, and the consequent increase in the effective size of the atom may tend to reduce the viscosity. We found no evidence of such change: it is probably too small for measurement, by reason of the small number of excited atoms.

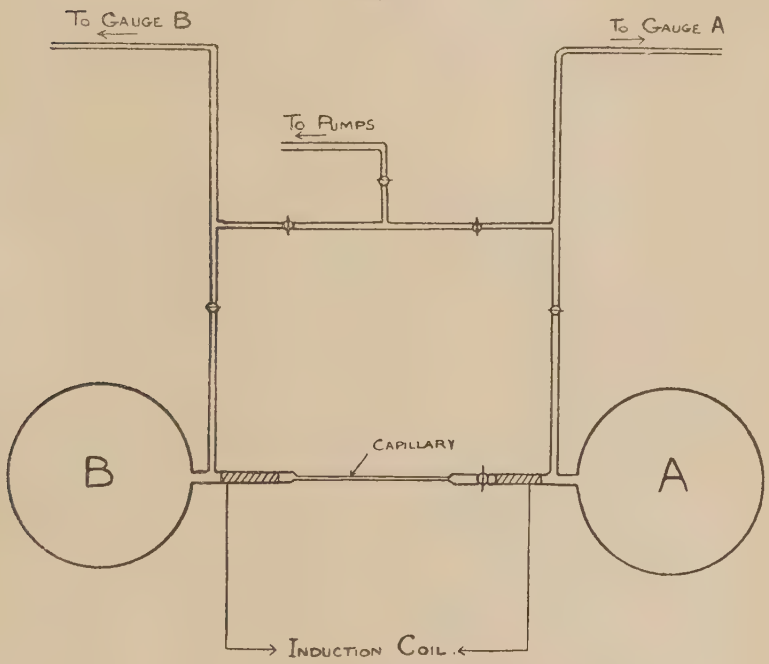
I.

On the experimental side the outstanding difficulty of the measurements lies in the disappearance and in the emission of gas during the discharge. So long as this occurs, the records of the pressure changes are no guide to the amount of gas flow through the capillary tube. In the first form of our apparatus the discharge tube was formed by two flasks connected by a fine capillary, and a McLeod gauge was connected to only one of the flasks; it was therefore impossible to check whether the total amount of gas remained constant. A second gauge was added, and revealed that both absorption and emission of gas occurred. No glass taps had been used, and mercury seals were used to control the flow. As the glow of the discharge passed over this mercury some oxidation occurred, and the seals were therefore replaced by taps. The gas continued to disappear, and the platinum-wire electrodes were next removed and replaced by large external electrodes of tinfoil wrapped round the tubes in the way described by Manley. The final form of the apparatus is shown in fig. 1. A, B are two bulbs of about 500 c.c. capacity, and some P_2O_5 is kept in a small bulb attached to each. They are connected by a fine capillary tube C, 4·10 cm. long and 0·0791 mm. internal diameter; two other tubes were also used. The discharge occurred in A, B, and C, and the pressures in A and B were measured before and after a time of flow through C by connecting each bulb with its gauge. The relative volumes of bulb and gauge were known, and the proper allowance was made for the pressure in the gauge before connexion was made with its bulb.

* Communicated by the Author.

Much attention has been given to the problems of the changes in gas-pressure, but the process has not yet been followed in the way which this apparatus permits. We have therefore made a number of measurements with gas-pressures from 0·01 mm. to 5·0 mm., and with currents of from 5 to 40 milliamperes, running from an induction coil for many hours at a time. It was found that the pressure

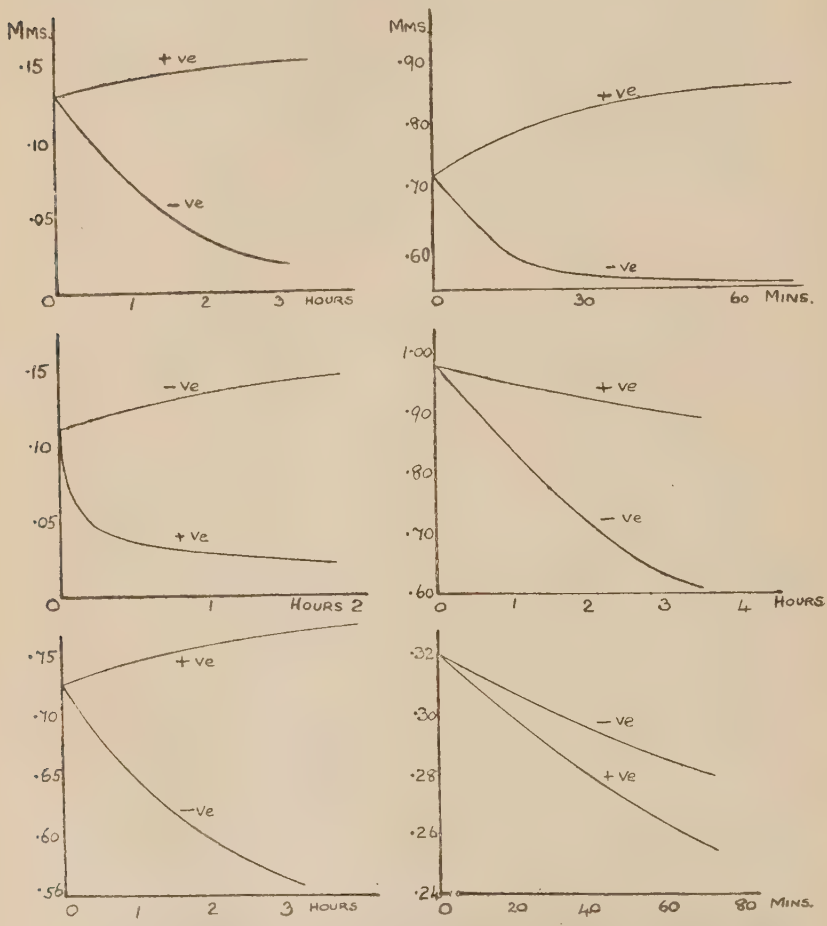
Fig. 1.



sometimes rose on the cathode side, sometimes fell; often it fell on both sides, and sometimes it remained constant. Examples of these changes are given in the small graphs in fig. 2. The changes are found to follow in every case an exponential law; some we have tested were records for every 30 minutes during 12 hours' discharge. When an increase of pressure occurred on one side, it tended to a maximum value; when gas disappeared, on the other hand, a minimum was never reached, because the pressure became so low that the discharge ceased. The current was kept roughly constant during each experiment by frequent adjustment of the primary resistance. It is possible to calculate, from the data

given later, how much gas has flowed from one side to the other during these experiments : but the flow is very slow indeed, and the correction does not affect the general form of the curves shown.

Fig. 2.



Absorption of gas was especially marked if there was a trace of solid impurity in the tube. It occurred sometimes when the tube had been very carefully cleaned, and the gas was in contact only with the glass, with a very little tap-grease and with P_2O_5 (the whole apparatus was made of glass). It was very much reduced when outside electrodes were introduced, and in the final apparatus it occurred on an average during only one-quarter of all the observed discharge

periods. (It has been recorded by Hill * that gas disappears even during an electrodeless discharge, but in his experiments the current passed for a shorter time, and it is probable that the glass reaction was not then complete ; some of the present discharge lasted for more than 20 hours, exclusive of intervals.) There was no obvious cause for the change when a period of absorption occurred. The only factor not completely examined was the character of the current from the induction coil ; the amount of the current was kept constant, but there were appreciable variations in the character of the make and break of the coil, and the voltage across the tube was not constant. Final cases of absorption were most common with oxygen, which suggests chemical action.

II.

The flow experiments were made with four different gases —chemically pure nitrogen, commercial oxygen, air, and a mixture of 75 per cent. argon with 25 per cent. nitrogen and a trace of oxygen. The whole apparatus was exhausted, using a mercury-vapour pump, before each gas was introduced. The main bulbs were so mounted that they could be surrounded by an electric furnace and maintained at 300° C. during evacuation. Pure phosphorus pentoxide, occasionally renewed, was kept in the apparatus throughout the experiments. In order that the discharge could pass, the pressures were within the limits 0·01 mm. and 2·0 mm. of mercury. Readings of the pressures were taken at intervals of half an hour or an hour, sometimes alternating periods of flow during discharge with periods of ordinary flow, and at other times taking longer periods of the two kinds of flow. Except when absorption or emission of gas occurred, there was no difference between the rates of flow in the two cases within less than 5 per cent. A typical set of readings for each of three gases is shown in the tables. In every case the pressures before and after the flow on each side of the capillary were read, and when slight differences occurred between the two changes of pressure (after allowing for the relative volumes of the two flasks) the mean was taken: when the differences were large, absorption had occurred, and the readings were rejected. In each set the mean pressure is approximately the same throughout, and therefore the "conductance" of the tube, Knudsen's "T" (see below), should be constant whether the flow be viscous or molecular. Its apparently excellent constancy in the

* Hill, Proc. Phys. Soc. xxv. 1912, p. 35.

oxygen set is fortuitous, for the pressure changes at the end of the set are so small that an error of 5 per cent. is possible. It is clear from the tables that the electric discharge has no effect upon the flow, whatever its direction; it is marked +ve when the positive electrode is on the side of higher pressure.

The pressures p_1, p_2 are the initial pressures in the two bulbs; p_1', p_2' are the pressures after time t. The figures in the last column are proportional to the "conductance," and are obtained by dividing p_1-p_1' by the time in minutes and by the mean difference of pressure, $\frac{1}{2}(p_1+p_1')-\frac{1}{2}(p_2+p_2')$.

p_1 mm. Hg.	p_1' mm. Hg.	p_2 mm. Hg.	p_2' mm. Hg.	t. minutes.	Current.	T.
Air.						
0·730	·702	0·027	·046	42	none	88.10^{-5}
·702	·670	·047	·072	56	+ve	88 „
·670	·649	·072	·090	45	none	81 „
·649	·628	·098	·115	51	−ve	75 „
·628	·599	·140	·165	82	none	77 „
·597	·548	·163	·150	32	+ve	absorption
Argon and Nitrogen.						
·982	·944	·126	·160	92	none	50.10^{-5}
·750	·714	·122	·152	120	+ve	49 „
·714	·681	·152	·181	120	−ve	53 „
·645	·627	·202	·216	75	none	54 „
·604	·584	·216	·232	100	−ve	52 „
·584	·557	·231	·253	150	+ve	53 „
·560 *	·549	·254	·263	70	none	51 „
Oxygen.						
1·931	1·780	·892	1·921	200	none	83.10^{-5}
1·803	1·698	1·019	1·108	180	+ve	84 „
1·662	1·570	1·091	1·095	120	+ve	absorption
1·567	1·350	1·094	1·112	300	−ve	„
1·352	1·312	1·107	1·141	220	none	88.10^{-5}
1·287	1·266	1·144	1·160	180	−ve	92 „
1·262	1·250	1·165	1·175	160	none	87 „

Current ..... Between 6 and 10 milliamperes in each case.
Volumes ..... V_1: 394 c.c.; V_2: 504 c.c.
Temperature ... 18° C.

* The composition of the argon mixture was slightly changed towards the end of this set of consecutive periods, because of the different rates of flow of argon and of nitrogen.

III.

At the pressures which we have used, the coefficient of viscosity changes rapidly with pressure under normal conditions, and the term becomes meaningless at the lowest pressures. As the published data in this region are few, and there are none at all for mixtures other than air, we have recorded these results in full.

The usual expressions for the quantity of gas, Q, flowing through a capillary tube in one second, in terms of the mean pressure p between its ends, are these :

$$T = \frac{Q}{p_1 - p_2} = \frac{\pi r^4}{8L} \frac{pr}{\eta}; \quad . \quad . \quad . \quad . \quad . \quad (1)$$

(Poiseuille—viscous flow at ordinary pressures.)

$$T = \frac{Q}{p_1 - p_2} = \frac{4\sqrt{2\pi}}{3\sqrt{\rho}} \frac{r^3}{L}. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

(Knudsen—molecular flow at low pressures.)

Knudsen * has suggested that for intermediate pressures the formulæ can be combined in the following way :

$$\frac{Q}{p_1 - p_2} = \frac{\pi r^4}{8L} \frac{pr}{\eta} + \frac{4\sqrt{2\pi}}{3\sqrt{\rho}} \frac{r^3}{L} \cdot \frac{1 + 2\sqrt{\rho} \cdot pr\eta^{-1}}{1 + 2{\cdot}47\sqrt{\rho} \cdot pr\eta^{-1}}. \quad (3)$$

Another, more empirical, expression has been given by Todd † in terms of a variable coefficient of velocity η_p :

$$\eta_p = \eta(1 - e^{-kpr}). \quad . \quad . \quad . \quad . \quad . \quad (4)$$

We find, by revising Todd's results, that they can equally well be represented by the formula

$$\eta_p = \eta \cdot \frac{pr}{pr + k}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and this can be put into a form which is similar to Knudsen's, and is generally more useful,

$$T = \frac{Q}{p_1 - p_2} = \frac{\pi r^4}{8L} \frac{pr}{\eta} + K \cdot \frac{r^3}{L}. \quad . \quad . \quad . \quad (6)$$

This form is to be preferred, because no physical meaning can be given to the term viscosity when intramolecular collisions are negligible compared with boundary collisions.

* Knudsen, *Ann. d. Phys.* xxviii. p. 75 (1909).
† Todd, Proc. Durham Phil. Soc. vi. p. 8 (1920).

It is unfortunate that this formula cannot also be tested by Knudsen's more extensive set of results; but Knudsen does not record the values of p_1 and p_2 separately. An important difference between the expressions (3) and (6) is that the former indicates the existence of a minimum value of T at a certain pressure. We have calculated the T, p curves from Todd's results, and, though they show less consistency than Knudsen's, it is clear that for five different tubes, and through a complete range of pressures, there is no sign of this minimum. It may be noted that the experiments of Timiriazeff*, by a rotating cylinder method, show no minimum in the variation of a similar function.

Both expressions are only strictly applicable (without detailed integration along the tube) when p_1-p_2 is very small, unless the T, p curve shows little curvature. For if the curvature is considerable, the apparent mean point for two widely different pressures must differ very much from the actual mean point deduced from the graph. The experimental results here recorded support the view that there is no great curvature and probably no minimum in this graph; and they support very clearly the general assumption that Q depends only upon p_1-p_2 and p_1+p_2, and not upon p_1 and p_2 separately.

IV.

A preliminary analysis may be made of the state of the gas when a discharge is passing. Molecules, atoms, ions, and electrons are all present. The tube is filled with a sensibly uniform positive column, in which the electric force is uniform, and, according to J. J. Thomson's experiments by the positive ray analysis method, there are no negative ions present. There is no evidence of a high temperature in the gas, and the molecular dissociation, like the ionization and excitation of both atoms and molecules, is mainly due to electronic collisions, and very little to intramolecular ones. The influence of this dissociation on the viscosity, at the higher pressures, may be roughly estimated in the following way.

Let the diameters and masses of the molecules and atoms be d_m, m, and d_a, $\frac{1}{2}m$ respectively. The viscosities of the molecules and atoms separately may be given by

$$\eta_m = \frac{mv_m}{2{\cdot}88\pi d_m^2}, \qquad \eta_a = \frac{\frac{1}{2}mv_a}{2{\cdot}88\pi d_a^2}.$$

* Timiriazeff, *Ann. d. Phys.* xl. p. 971 (1913).

We may write

$$\tfrac{1}{2}mv_m^2 = \tfrac{1}{2}\cdot\tfrac{1}{2}m\cdot v_a^2\,;$$

and for the relation between the two diameters we note that Rankine's * calculation for a molecule made up of two rare gas atoms gave

$$d_a^2 = 0{\cdot}61dm^2,$$

and we assume the same relation here. The result is then

$$\eta_m = 0{\cdot}86\eta a.$$

If we suppose that one-half of the molecules are dissociated —a very large over-estimate,—the viscosity of the mixture can be calculated by one of the two usual expressions for gas mixtures, and we have taken that due to Puluj †. We neglect the tendency of two atoms to re-unite, and also the forces which divide them again. The result so found is

$$\eta = 1{\cdot}10\eta_m,$$

so that this large amount of dissociation produces a slight increase in viscosity. There is a small rise in temperature which acts in the same direction, and there is an increased force of repulsion between such atoms as are positively charged, also tending to increase the viscosity.

In the Bohr model of the atom the excited and luminous atom is distinguished by an outer electron or electrons circulating in a very much enlarged orbit, and the atom may therefore be increased in area very greatly. This would lead to a large decrease in viscosity, were it not that the orbits in this model are plane ones and the change in the mean collision area presented by the molecule is less than the change in the area enclosed by the orbit. Moreover, the number of atoms affected at any instant, both as to excitation and to ionization, is a very small fraction of the total number present. If the pressure is 1 mm., and a current of 10 milliamperes passes through the capillary tube, mostly carried by electrons, then a simple calculation shows that for every molecule in the tube about 100 electrons pass through the tube in every second. If the excitation time for the molecule is of the order of 10^{-8} second, then very few will be in that enlarged state at any instant.

The direction of the discharge through the flowing gas

* Rankine, Proc. Roy. Soc. xcviii. p. 360 (1921).

† Puluj, *Wien. Ber.* lxxix. p. 112 (1879); see also Thomson, *Ann. d. Phys.* xxxvi. p. 815 (1911), and Gille, *Ann. d. Phys.* xlviii. p. 799 (1915).

must also influence the flow, for it governs the motion of the electrons, and we have not yet considered the electron molecule collisions. The mean velocity of the electrons in the discharge tube has been examined by Compton *, and on the basis of his theory we find that the total contribution of their momentum to the movement of the molecules is less than could be observed in our experiments. The experimental results actually show no change in the rate of flow when the current is reversed. J. J. Thomson † has indicated one further cause of pressure variations within a discharge tube—the flow of positive ions; but this effect is confined to the dark space, and is not measured by the present apparatus.

In the case of the lowest pressures, the molecular flow of atoms and of molecules may proceed independently. Suppose that the inflow pressure, p, is made up of p_{1a} due to atoms and p_{1m} due to molecules, and similarly with p_2. Then, according to Knudsen's method (Knudsen did not consider mixtures), the quantities flowing through the capillary are

$$Q_a = \frac{k}{\sqrt{\rho_a}}(p_{1a} - p_{2a})$$

and

$$Q_m = \frac{k}{\sqrt{\rho_m}}(p_{1m} - p_{2m}),$$

where k depends only on the dimensions of the tube. The total quantity is given by

$$Q = Q_a + Q_m = k\left\{\frac{p_{1a} - p_{2a}}{\sqrt{\rho_a}} + \frac{p_{1m} - p_{2m}}{\sqrt{\rho_m}}\right\}.$$

Making the same assumptions as in the previous case of viscous flow, we now write

$$\rho_m = 2\rho_a \quad \text{and} \quad p_a = 2p_m = \tfrac{2}{3}p_1,$$

and the formula becomes

$$Q = 1{\cdot}28\frac{k}{\sqrt{\rho_m}}(p_1 - p_2),$$

The effect of ionization is therefore to *increase* Q, and this is analogous to a decrease of viscosity. In this case, then, the effects of ionization and excitation are in the same direction, and we might expect a small measurable change at the lowest pressures for large currents.

* Compton, Phys. Rev. xxii. p. 333 (1923), and xxiv. p. 507 (1924).
† Thomson, Phil. Mag. xlviii. p. 1 (1924).

Summary.

1. Measurements have been made of the molecular and viscous flow of gases in fine capillary tubes at low pressures.

2. The rate of flow is found to be unaffected, to within less than 5 per cent., by an electric discharge passing through the flowing gas. A theoretical discussion suggests that an effect is to be expected with diatomic gases at very low pressures.

3. Observations have been made of the disappearance and emission of gas in discharge tubes. The change of pressure follows an exponential law when it occurs, and under special circumstances there may be no change.

XXXIX. *The Optical Anisotropy of some simple Inorganic Gaseous Compounds.* *By* K. R. Ramanathan, *M.A., D.Sc., and* N. G. Srinivasan, *B.Sc., Physics Department, University College, Rangoon* *.

Introduction.

FROM the time that Lord Rayleigh discovered the imperfection of polarization of the transversely scattered light in gases, it has been the hope of physicists that some time or other it would lead to important knowledge regarding the structure of atoms and molecules. In his recent work on the doubly refracting properties of typical inorganic crystals, W. L Bragg † has made use of the idea of the mutual influence of the polarization of the different atoms of the crystals, and has deduced results which are in general agreement with observation. In this work, Bragg assumes with Wasastjerna that the atoms are in an ionized condition: that is, they have given up or taken in a sufficient number of electrons so that the electronic structure of each ion approaches closely that of the nearest inert gas. He further assumes that each ion by itself can be considered optically isotropic.

One of the authors has recently shown that the optical anisotropy of some of the common inorganic gases ‡ which is evidenced by the imperfection of polarization of the transversely scattered light in these gases, can be likewise explained if we take into account the mutual influence of the

* Communicated by the Authors.

† Proc. Roy. Soc. A, vol. cv. p. 370 (1924).

‡ Proc. Roy. Soc. A, vol. cvii. p. 684 (1925).

polarizations of the different atoms in the molecule. The work has later been extended to the organic molecules benzene and cyclohexane, but in all the cases that have been hitherto examined the gases are of the "homo-polar" or shared-electron type.

With a view to getting some idea of the optical anistropy of the "hetero-polar" molecules, experiments have been made on a few simple hydrides. The inert gases are known to possess a high degree of symmetry, and the experiments of Lord Rayleigh * on argon and of Cabannes and Lépape on xenon and krypton † show that the optical anistropies of these molecules are very small, the values of the imperfection of polarization of the transversely scattered light in these gases being respectively ·0046, ·0055, and ·0055. Hydrides of elements adjoining the inert gases, like those of the halogens, would, it is believed, assume electronic structures similar to those of the inert gases, with perhaps a slight deformation of the symmetrical structure caused by the presence of the hydrogen nuclei. The gases CH_4, NH_3, H_2O may be expected to approach neon, while SiH_4, PH_3, H_2S, and HCl would approach argon.

In the following paper the results obtained with ammonia, sulphuretted hydrogen, and hydrochloric acid are described and discussed.

Experimental.

The apparatus employed was of the usual type, being a rectangular metal cross-tube of 5 cm. internal diameter. Each arm of the cross was 27 cm. in length. The tube was coated inside with black enamel which on heating gave a hard glassy coating. Three ends of the cross were closed with plane glass plates sealed on with sealing-wax or hard paraffin, while the fourth end was closed with a metal cap. An oblique metal plate with a uniform glassy coating of black enamel was placed near the closed end so as to reflect away any stray light which might reach that end. Suitable blackened metallic apertures were placed in the different arms so as to shut out stray light. The cross was also provided with two side tubes, one to serve as an inlet for the gas and the other to serve as an exit.

After drying and cleaning, the apparatus was exhausted by means of a pump and the dry dust-free gas was slowly let in. During the experiment a continuous stream of the

* Proc. Roy. Soc. A, vol. xcviii. p. 57 (1920).
† *Comptes Rendus*, clxxix. p. 325 (1924).

gas was kept running. The measurements of depolarization were made in the usual manner by means of a Wollaston double-image prism of quartz and square-ended nicol with a small low-power reading telescope placed behind the nicol.

The pure gases were prepared in the following manner :—

(a) *Hydrochloric acid gas.*

By the action of strong sulphuric acid on sodium chloride. The gas was dried by passing over fresh phosphorus pentoxide.

(b) *Hydrogen sulphide.*

By heating antimony trisulphide with concentrated hydrochloric acid. It was found that free evolution of gas was helped by mixing the antimony sulphide with clean sand. The gas was first bubbled through water to remove the acid spray and then dried over phosphorus pentoxide.

(c) *Ammonia.*

By warming a concentrated solution of ammonia. The gas was passed through a lime tower to remove moisture.

Usually for observations on the scattering of light in gases, the dust particles that are invariably present are removed by slow passage through a tube packed with cotton-wool. As it was, however, found that cotton-wool was slowly attacked by HCl, it was replaced throughout the experiments by clean dry asbestos wool, which was found to be a good substitute.

Error due to convergence of the Incident Rays.

Before discussing the experimental results, it is worth while to consider a source of error which, while unimportant when measuring the imperfection of strongly depolarizing substances, becomes of considerable importance when small values of depolarization are measured *. When the incident beam is focussed by means of a lens, and the imperfection of polarization is measured in a direction perpendicular to the average direction of the beam, the value obtained would be different from what it would be if the beam were strictly parallel. The error would be greater the greater the convergence of the beam. To find its amount, consider a beam of plane polarized light with its electric vector parallel to OZ moving along the X-axis. When observed along OY, let the Z-component of the intensity of the scattered light be A and the X-component B ; then, when the incident light

* Lord Rayleigh, Proc. Roy. Soc. A, vol. xcv. p. 161.

is unpolarized, the components will be A + B and 2B respectively. If the direction of observation be changed by an angle θ, the principal components in a plane perpendicular to the scattered ray will become A + B and B $(1 + \cos^2\theta)$ + A $\sin^2\theta$ respectively, and thus the observed ratio of the weak component to the strong will be

$$\rho_\theta = \frac{A\sin^2\theta + B(1+\cos^2\theta)}{A+B} = \frac{2B + (A-B)\sin^2\theta}{A+B},$$

which differs from ρ, the value in a transverse direction, by $(A-B)\sin^2\theta/(A+B)$.

In our present case, $\sin\theta$ varies from $-a/d$ to a/d where $2a$ is the aperture of the lens, and d is the distance from the lens at which the rays are focussed *.

We have, therefore, to find the average values of ρ_θ when θ varies through this range. A simple integration and averaging give for the ratio of the weak component to the strong in a direction perpendicular to the average direction of the beam

$$\frac{H}{V} = \frac{2B + (A-B)\sin^2\theta/2}{A+B}.$$

In the case of a gas producing an imperfection of polarization of 0·01 in a strictly perpendicular direction, the error caused by the non-parallelism of the incident rays will be as much as ·0038 when θ is 5° and ·0014 when θ is 3°.

Similar errors will be caused by a wrong adjustment of the double-image prism and by the direction of observation not being exactly perpendicular to the incident beam. The former error can be avoided by a careful adjustment of the double-image prism; the latter is usually small in visual observations, but it is one to be borne in mind when measurements are made photographically where the temptation is to use a large aperture in order to secure economy of light.

Results.

The observed value of the ratio of the weak component to the strong in the transversely scattered light in each of the gases HCl, H_2S, and NH_3 was found to be the same, namely ·010. The measurements were repeated on different days, and consistent results were obtained. There was no evidence of fog formation in any of the cases. In changing from one gas to another the whole apparatus was overhauled and

* With the small angles usually employed, the distinction between $\sin\theta$ and $\tan\theta$ may be dropped.

thoroughly cleaned, and the inside of the tube was repainted. The maximum angular divergence of the rays from the axis was measured to be 3°·8, and hence the error due to the non-parallelism of the incident rays was ·002. If we subtract this from the value obtained above, we get for all the three gases the corrected value ·008.

It is remarkable that the values of ρ for all these gases should be so low, and that they should all be equal to each other. They are also of the same order of quantities as the values obtained for the inert gases. As mentioned above, Lord Rayleigh obtained the value ·0046 for argon, which, however, has not been corrected for the non-parallelism of the incident rays. Lord Rayleigh estimated the extreme divergence of the incident rays from the axis to lie between 3° and 4°, and the angle subtended by the aperture of the camera was of the same order. The corrected value would be only about ·0025. Whether this residual effect does exist or not is worth re-examination.

It is now generally believed that in hydrochloric acid gas the electron belonging to the hydrogen atom has gone over to the chlorine atom to form one of its outermost orbits, thus completing the argon configuration, and similarly in sulphuretted hydrogen the two electrons from the hydrogen atoms have been transferred to the outermost orbits of sulphur. The smallness of depolarization of these gases supports this view. Likewise in ammonia, the additional electrons belonging to the three hydrogen atoms may be looked upon as having been transferred to the nitrogen to complete the neon configuration. Although no measurements of the depolarization of the transversely scattered light in neon are available, it may be expected to be small.

The cases of carbon monoxide and nitrogen are interesting. Langmuir and others have suggested that the configurations of the outer electrons of these gases are similar. If that is so, we expect that the optical anisotropies of the two gases should be nearly the same. Visual measurements made with sunlight at Calcutta show that carbon monoxide shows a depolarization of 3·4 per cent., while for nitrogen Lord Rayleigh * obtained the value 4·06 per cent. by the photographic method. On the other hand, if we calculate the depolarization of nitrogen from the visual measurements of Raman and Rao † on air (4·37) and oxygen (8·4), we obtain the value 3·5 per cent. For purposes of comparison

* Proc. Roy. Soc. A, vol. xcvii. p. 435 (1920).
† Phil. Mag. vol. xlvi. p. 427 (1923).

it is better to choose the values obtained by the same method, and the closeness of the values obtained by the visual method is very striking.

Summary.

In the foregoing paper, measurements of the depolarization of the light scattered by the gases hydrogen chloride, sulphuretted hydrogen, and ammonia are described, and the results obtained are discussed in their relation to the structure of the molecules. The depolarization in a direction perpendicular to the incident beam was in all cases the same, namely ·008, indicating a high degree of optical symmetry. The value of the anisotropy supports the view that in these gases the electrons belonging to the hydrogens have gone over to the outer orbits of the heavier atoms, in order to complete the electronic structure characteristic of the nearest inert gas. It is also pointed out that the values of the depolarization of nitrogen and carbon monoxide, both obtained visually, have practically the same value, supporting the view that the configurations of the outer electrons of these molecules are similar. The error caused in the measurement of the depolarization of the light scattered by substances owing to the non-parallelism of the incident light is discussed.

XL. *Some Considerations of the Reaction Constant Equation, and a Simple Method of determining the End Point.* *By* Robert Christie Smith, *Carnegie Teaching Fellow, University of Glasgow* *.

IN the determination of the velocity constant for a monomolecular reaction use is made of the equation

$$k=\frac{1}{t}\log\frac{a}{a-x}.$$

For a practical solution of this equation it is necessary to determine the concentrations "a" and "x," or at least numbers proportional to them. This is usually done by a series of measurements (titrations, polarimetric readings, etc.) commencing with the first taken immediately on mixing the reactants and ending with the final reading taken on completion of the reaction. To obtain the final reading it is necessary either to weigh a sample of known purity (*e. g.* of the ester, in a hydrolysis with acid) or wait at least 48 hours till the reaction is completed. It is, however,

* Communicated by the Author.

possible to obtain simply the required end point from the following considerations.

If $\tau_0 . \tau_1 . \tau_2 \ldots\ldots \tau_r \ldots\ldots \tau_\infty$ denote the readings obtained in the usual manner, it is possible to construct the following series from it.

$$\tau_1-\tau_0=T_1, \qquad \tau_n-\tau_0=T_n,$$
$$\tau_2-\tau_0=T_2, \qquad \tau_\infty-\tau_0=T_\infty,$$

when the equation for a monomolecular reaction becomes

$$k=\frac{1}{t}\log\frac{T_\infty}{T_\infty-T_n},$$

i. e. $$(e^k)^t=\frac{T_\infty}{T_\infty-T_n} \quad \text{or} \quad (e^{-k})^t=1-\frac{T_n}{T_\infty};$$

hence $$(e^{-k})=\left(1-\frac{T_n}{T_\infty}\right)^{t_n}=\left(1-\frac{T_{n+1}}{T_\infty}\right)^{t_{n+1}}=\ldots\ldots$$

If $t_{n+1}=2t_n$, then

$$\left(1-\frac{T_n}{T_\infty}\right)^2=\left(1-\frac{T_{n+1}}{T_\infty}\right),$$

or solving

$$T_\infty=\frac{T_n^2}{2T_n-T_{n+1}}.$$

Hence it is possible by calculation to obtain the "end point" from two values obtained at specified times such that the one time is half the other. It is to be noted that while the probability is that if a constant value is obtained for T_x then the reaction is monomolecular, but this cannot be strictly proved mathematically.

It is not possible for accurate results to be obtained by readings taken immediately the reaction starts, as at this point, besides the readings being as a rule slightly irregular, the value $(2T_n-T_{n+1})$ is small and any absolute error therein is magnified in the determined end point. This is most easily demonstrated if the constant and end point are assumed and the values T_n and T_{n+1} are calcu ated.

E.g., let $k=0{\cdot}0023$ and $T_\infty=20$,

then $$T_n\log\frac{20}{20-T_n}=0{\cdot}01 \quad \text{for} \quad t=10,$$

$$T_{n+1}\log\frac{20}{20-T_{n+1}}=0{\cdot}02 \quad \text{for} \quad t=20.$$

With four-figure logarithms $2T_n-T_{n+1}=0{\cdot}110$.

With eight-figure logarithms $=0{\cdot}0051813$.

However, as time goes on the value calculated by four-figure logarithms (which usually covers the accuracy of the titration etc.) becomes constant and dependable, as seen from the results in Table II. A theoretical set of results are given in Table I.

TABLE I.

Test equation.—Constant = ·015. End point = 20.

Value of x at			4 fig. logs.
10 mins.	= 2·7866333		
		= 19·94623	19·96
20 „	= 5·1849537		
		= 20·00102	20·00
40 „	= 9·025789		
		= 19·99996	20·06
80 „	= 13·978334		
		= 19·99992	20·01
160 „	= 18·186976		

TABLE II.

Actual results.

End point.	
Calculated.	Found.
3·48	3·47
3·64	3·61
8·58	8·59

TABLE III.

Effect of error in end point value on K.

End point value = 21.		= 19.
K = ·01426	at 10 mins.	·01585
·01416	20 „	·01593
·01406	40 „	·01613
·01370	80 „	·01664
·01257	160 „	·01972

Correct value = 20 as in Table I.

The method can be extended to bimolecular etc. reactions, but the expression for T_∞ becomes more complicated.

Again considering the equation,

$$k = \frac{1}{t} \log \frac{T_\infty}{T_\infty - T_n}.$$

If there is an error "α" in the end point it becomes

$$k = \frac{1}{t} \log \frac{T_\infty + \alpha}{T_\infty + \alpha - T_n}.$$

As this fraction $\left(\frac{T_\infty}{T_\infty - T_n}\right)$ is always greater than 1, the addition of an equal amount to the numerator and denominator will decrease its value, and as it becomes greater the decrease will become greater, and similarly if the error is negative its value will be increased. Hence in the first case, instead of a constant k, a series of decreasing values, and in the second a series of increasing values will be obtained. If, therefore, the reaction is known to be monomolecular the final reading T_∞ can be obtained by a method of trial and error. The effect can also be shown graphically by plotting "t" against $\left(\log \frac{T_\infty}{T_\infty - T_n}\right)$.

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University of Glasgow.

XLI. *The so-called Positive Photo-Electric Emission (Inverse Effect), and the Reality of the Sub-Electron.* *By* Edward J. Lorenz *.

I. *Introduction.*

A FEW observers have reported the discharge of positive electricity produced by ultra-violet light. Dember † found that a metal plate exposed to ultra-violet light *in vacuo* had the power to communicate a positive charge to a receiving cylinder when the proper accelerating field was applied. His experiments have recently been repeated by Du Bridge ‡, who reports that Dember's results can be entirely accounted for on the basis of the photo-electric effect produced on the collecting cylinder by scattered ultra-violet light against which no precautions had been taken.

* Communicated by Prof. R. A. Millikan.
† Dember, *Ann. der Phys.* iii. p. 137 (1909).
‡ Du Bridge, Phys. Rev. p. 201 (Feb. 1925).

His conclusions are: "there is no measurable photo-electric production of either gaseous or metallic positive ions by the range of wave-lengths emitted by the quartz mercury lamp."

R. Bär and F. Luchsinger *, working with small particles of paraffin and selenium in a Millikan electron apparatus, found that some of the particles showed the inverse effect—that is, they became charged negatively when illuminated by ultra-violet light. This has been construed by some workers as indicating the discharge of positive electricity. However, as they were only using the ultra-violet light to charge up their particles in order to measure the charge communicated, and were not interested in the source of the photo-electrons, it is natural to assume that no special precautions were taken against the light striking the metallic plates of the condenser. The photo-electrons liberated from these metal surfaces being caught by the paraffin and selenium particles would make it seem as if the particles had lost a positive charge. S. Taubes †, working in the same laboratory as Luchsinger and Bär and presumably with the same apparatus, reported this inverse effect when dealing with particles that had a large positive charge, and showed that it is due to the photo-electrons given off by the condenser plates, for when these were coated with paraffin the inverse effect entirely disappeared.

M. Hake ‡, working at Vienna and using a diminutive Millikan electron apparatus designed by Prof. Ehrenhaft, has recently reported results on nineteen different materials. He found that metals show both the inverse and the normal effect, depending on the gas in which the metal particles are suspended, and that some insulators, for example glycerine, always show the inverse effect in all gases. Wasser §, working in the same laboratory as Hake, gives results on mercury drops in N and CO_2. He claims that drops of larger radius than $1{\cdot}9 \times 10^{-5}$ always show the normal effect, that those between 1·1 and $1{\cdot}9 \times 10^{-5}$ cm. show both the normal and the inverse effect, while those of smaller radius than $1{\cdot}1 \times 10^{-5}$ cm. always show the inverse effect.

The following investigation was undertaken to test the correctness of the foregoing conclusions, and to determine whether the changes in charge experienced by minute mercury droplets are of a magnitude corresponding to the

* F. Luchsinger, *Ar. Sc. Phys. et nat.* i. p. 544 (1919); R. Bär and F. Luchsinger, *Phys. Zeit.* xxii. p. 227 (1921).

† S. Taubes, *Ann. der Phys.* vi. p. 646 (1925).

‡ M. Hake, *Zeit. f. Phys.* Bd. xv. Heft 2–3 (1923).

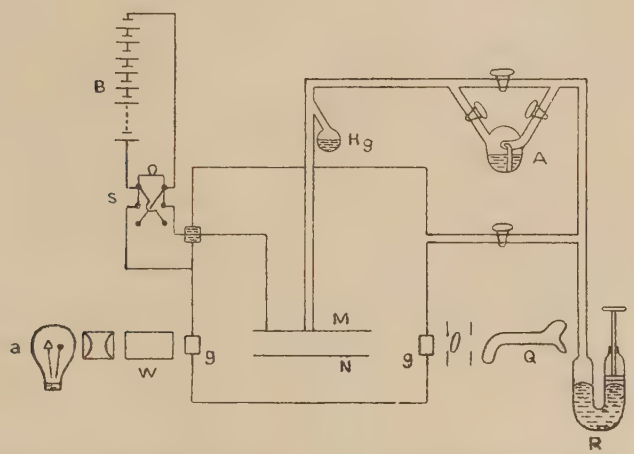
§ E. Wasser, *Zeit. f. Phys.* Band xxvii. Heft 4 (1924).

electronic charge or to a charge smaller than this, as the Vienna physicists have maintained *.

II. *Method.*

The apparatus used in the work consisted of a Millikan condenser such as has been used by Millikan and his pupils during the past fifteen years. Fig. 8, p. 118 of 'The Electron' †, by Millikan, shows a cross-section. Fig. 1 shows a diagrammatic scheme of the apparatus. The illumination was pushed to its limit. The light which entered the window "*g*" was produced by a 500 c. p. point-light, the rays of which were concentrated by a

Fig. 1.



powerful condensing lens. At 90° to this window was a quartz window through which a beam of ultra-violet light which had been concentrated by a quartz lens and passed through the proper diaphragms so as to avoid striking the plates M and N, was allowed to pass. This ultra-violet light could be turned on and off by raising or lowering a shutter operated by a foot pedal.

The gases used were washed and filtered by slowly bubbling them through water, then through concentrated H_2SO_4, and finally passing them through a long tube filled with $CaCl_2$. The ends of the tube were plugged with glass wool. The nitrogen was also washed in a tower containing copper spinnings over which a solution of NH_4OH and

* Phil. Mag. vol. xlix. (April 1925).

† Rev. Ed., University of Chicago Press, 1924.

NH_4Cl continuously passed. It was also bubbled through a bottle of strong KOH so as to remove any CO_2. Only three cubic centimetres per second passed ; this gave the cleansing agents ample time to act.

In making observations the substance under test was blown over from the atomizer A by means of a mercury compressing device R which allowed the gas to be taken from the test chamber and returned through the atomizer without any danger of being contaminated. In the case of mercury the drops were produced by substituting the mercury boiler Hg for the atomizer A. When the drops, whatever their nature, were observed through the telescope and the battery then connected, the charged particles were at once swept out of the field, only the neutral ones being left. With the field still on, the ultra-violet light was then directed upon the drops, and the speeds observed with the battery first connected one way, then the other. In order to test whether or not the rays from the quartz lamp had the power of ionizing the gas, drops that were normally very sensitive were charged and held suspended in the field of view by applying the proper potential difference. A narrow strip of opaque material was then placed across the quartz window so as to protect the drop from the direct influence of the ultra-violet light, but to allow the gas on either side of the drop to be illuminated With this arrangement, prolonged exposure to the ultra-violet light, for ten minutes or more, produced no change in the charge of the drop, thus proving that the gas around it was not affected by the ultra-violet light.

III. *Qualitative Results.*

Fifty drops of oil varying in apparent radius from 1·6 to 3×10^{-5} cm. were observed in air, N_2, H_2, CO_2, O_2, and He. *In no case was any effect observed. When the screens that kept the ultra-violet light off the plates were removed, the inverse effect was immediately detected.*

Fifty drops of glycerine of about the same range of diameters were observed in air, N_2, and H_2. *In no case was it possible to detect any effect. The removal of the screens shielding the plates again produced the inverse effect.*

A long series of experiments was conducted with Hg drops in air and in N_2. Fifty different drops of mercury, varying in apparent radius from 1·4 to $8·4 \times 10^{-5}$ cm., were illuminated with ultra-violet light more than 80 different times when neutral and when charged with various charges, sometimes positive, sometimes negative. *In no case was an increase of the negative or a decrease of the positive charge observed.*

Whenever a change occurred it was always of the normal type. The radii of these drops were computed by Millikan's* method. When Wasser's method is used they correspond to a range from ·95 to $8{\cdot}4 \times 10^{-5}$ cm. Both methods use the assumption (shown below to be incorrect) that the density of all the particles is 13·6. They differ only in that Wasser's computations depend upon the assumption of a somewhat incorrect law of fall, while Millikan's method avoids this source of error. Wasser's range was from ·7 to $3{\cdot}3 \times 10^{-5}$ cm. I have, therefore, worked over practically the same range of droplet-radii as did he.

Another method, and one which is, I think, an improvement upon the foregoing procedure, used by Wasser, was to charge the drops slightly by γ-rays and then adjust the applied potential so as to just balance the drop. In this way a single drop could be floated in the field of view for 30 minutes or an hour at a time, and thus the exposure time to the ultra-violet light increased. *In no case was an inverse effect noted.* Under this prolonged exposure to the ultra-violet light, drops that were ordinarily classified as insensitive sometimes charged up in the normal way. *When the screens that shielded the plates from the ultra-violet light were removed, the drops showed the inverse effect after a very short exposure.*

Our conclusions are that the inverse effect, reported by Hake and Wasser as indicating a discharge of positive electricity, has no real existence. It is a spurious effect produced by stray or scattered ultra-violet light striking the plates of the condenser and liberating photo-electrons, which are caught by the drop in the apparatus. The correctness of this conclusion is suggested by the dimensions of Hake and Wasser's condenser, namely $9 \times 9 \times 2$ millimetres. In such a condenser it is clearly extraordinarily difficult, if not altogether impossible, to make a concentrated beam of ultra-violet light pass through the 2-millimetre opening without its striking somewhere and scattering over the entire area of the plates. Our apparatus had the plates 15·3 mm. apart, and was therefore better suited for testing the effect of letting the light strike the drop alone, the plates alone, or both together.

IV. *Reality of the Sub-Electron.*

In the same region of radii in which Wasser finds that mercury droplets show the inverse photo-electric effect, he also finds that the charge or change of charge on the droplets

* Millikan, 'The Electron,' p. 104.

is far below the accepted value of the electron—that is, below $4{\cdot}77 \times 10^{-10}$ E.S.U.

In order to test whether or not changes of charge of smaller value than the electron are indeed ever produced by ultra-violet light, or otherwise, in drops of any size or kind, a long series of experiments was carried out. My results are in agreement with Wasser's in that the apparent charges obtained on some of the drops, using Wasser's method of computing, fall below $4{\cdot}77 \times 10^{-10}$ E.S.U. *But, the real test of the existence of the sub-electron in this experiment consists in finding whether all the charges obtainable on a given drop are exact multiples of the smallest charge which it is ever found to carry.* Millikan * has emphasized this in one of his recent papers.

The justification for the foregoing statement is that Millikan and many other workers have shown that the smallest charge caught on an oil drop or any other kind of particle *when ionization is produced in the surrounding gas* is always $4{\cdot}77 \times 10^{-10}$ E.S.U., or some multiple of this unit irrespective of the size of the drop. If, then, when we are dealing with a mercury droplet we find that the charge given to it by an electron caught *from the surrounding gas*, which has been ionized by γ- or X-rays, is exactly the same as the charge given to it by being illuminated by ultra-violet light, it follows that the latter charge has also the value $4{\cdot}77 \times 10^{-10}$ E.S.U. Any contrary results obtained on the basis of an assumed density must perforce be ascribed to a wrong assumption as to this drop-density.

In the accompanying Tables I., II., and III. the column headed $\frac{v_1 + v_2}{n}$ shows how perfectly the multiple relationship holds with precisely the same sort of drops used by Wasser, and obtained under precisely the same conditions that he used when he thought he got sub-electrons by the photo-electric process. Table I. shows results on a droplet that was very sensitive to ultra-violet light. Table II. shows results on a drop that showed only slight sensitivity. The results in Table III. were obtained with a drop that was not affected by the ultra-violet light, even after several minutes exposure. These three tables are typical of results that were obtained on at least twenty-five different drops that were tested for multiple relationship, about half of them in air and half in pure nitrogen. Some of these drops were carried through twenty changes of charge. In no case was the

* Millikan, Phys. Rev. p. 101 (July 1925).

variation of $\frac{v_1 + v_2}{n}$ more than 1·5 per cent. from the mean, even though the readings were taken merely with a stop-watch, and therefore not with very great precision.

TABLE I.

Sensitive drop. p 74 cm.

Change in charge produced by	Stop-watch Readings. T_g.	T_f.	Average. v_1.	v_2.	v_1+v_2.	n.	$\frac{v_1+v_2}{n}$.
	47·0	24·5	·01120	·02171	·03291	−1	·0329
U. V. L.		24·2	„	·02194	·03314	+1	·0331
Spontaneous	47·1	9·4	„	·05553	·06673	+2	·0334
Spontaneous.....	47·4	23·9	„	·02226	·03346	+1	·0335
U. V. L.		9·4	„	·05553	·06673	+2	·0334
U .V. L.		4·3	„	·12372	·13492	+4	·0337
	48·3						

Volts..... 1925 a $2{\cdot}3\times10^{-5}$
Distance between cross hairs... ·532 cm. e_1 7×10^{-10}
Distance between plates ..... 1·53 cm.

TABLE II.

Slightly sensitive drop. p 74·1 cm.

Change in charge produced by	Stop-watch Readings. T_g.	T_f.	Average. v_1.	v_2.	v_1+v_2.	n.	$\frac{v_1+v_2}{n}$.
	63·2	4·2	·00841	·12666	·1 507	−13	·0104
Spontaneous		9·7	„	·05484	·06325	− 6	·0105
U. V. L.		12·1	„	·04396	·05237	− 5	·0105
Spontaneous	64·0	15·9	„	·03325	·04166	− 4	·0104
U. V. L.		42·0	„	·01266	·02107	− 2	·0105
Spontaneous	61·6	242·0	„	·00219	·01060	− 1	·0106

Volts..... 900 a $2{\cdot}4\times10^{-5}$
Distance between cross hairs... ·532 cm. e_1 $4{\cdot}2\times10^{-10}$
Distance between plates..... 1·53 cm.

TABLE III.

Insensitive drop. p 74 cm.

Change in charge produced by	Stop-watch Readings. T	Tf.	Average. v_1.	v_2.	v_1+v_2.	n.	$\frac{v_1+v_2}{n}$.
		3·4	00232	·15647	·15879	+6	·0264
Spontaneous.....	228·8	10·6	,,	·05001	·05233	+2	·0262
Spontaneous.....	228·4	6·8	,,	·07823	·08056	+3	·0268
Radium.....		21·9	,,	·02429	·02661	+1	·0266
Radium		21·9	,,	·02429	·02661	−1	·0266
Spontaneous.....	228·6	10·6	,,	·05001	·05233	−2	·0262

Volts..... 1925 a $1{\cdot}5\times10^{-5}$
Distance between cross hairs... ·532 cm. e_1 $2{\cdot}6\times10^{-10}$
Distance between plates..... 1·53 cm.

Here, then, we have the proof that the smallest quantity of electricity that any drop takes on is $4{\cdot}77\times10^{-10}$ E.S.U., and that it is independent both of the mechanism of charging and of the size of the drop. The reason for the apparent appearance of smaller charges in Wasser's and Ehrenhaft's work is shown in the following section.

V. *Sizes and Densities of Drops.*

In calculating the radius of the drop, the equation

$$a=\sqrt[3]{\frac{3\mathrm{F}e_n}{4\pi g(\sigma-\rho)}\ \frac{v_1}{v_1+v_2}}$$

was used (Millikan, 'The Electron,' p. 104). "e" was placed equal to $4{\cdot}77\times10^{-10}$ E.S.U., since the multiple relationship had established the fact that the charges were all unitary charges, and since Millikan's work of the past fifteen years has fully established this value for the uni of charge. The results of this paper are, however, in no way different if a is computed from an approximate correction to Stokes's law and without any use of the value of e*. The

* Prof. Ehrenhaft is entirely in error in asserting that Millikan's results depend in any way upon the *assumption* either of a multiple relationship in drop-charges or a numerical value of e. *These are both direct experimental facts.* See Millikan, Phys. Rev. vol. xxvi. no. 1 (July 1925).

method adopted is merely the more convenient and the more accurate. No drops were used on which sufficient data had not been obtained to establish the multiple relationship so that v_2, the velocity under a known field, could be established for a single electron on the drop. Wasser* uses for obtaining a the corrected form of Stokes's law of fall, namely

$$\frac{4\pi a^3 \sigma g}{3} = \frac{6\pi a v_1 \eta}{1 + A\frac{e}{a}}.$$

He assumes, however, that A is a constant. As a matter of fact, in the region of radii in which he thinks he works, A varies from ·7 to ·98, as shown by Millikan†. While, however, Wasser's method and mine always agree quite closely for droplets which are actually spheres of mercury, his method yields apparent radii as much as 30 per cent. smaller than those given by my method for droplets which are not spheres of mercury. When calculated by Wasser's method our smaller drops are as small as those he uses. Either method, however, yields only the apparent size of the smaller drops, as we shall show that the density of these is very far from that of Hg.

In order to find the charge on the drops, the value of e_1 was first found by means of the equation

$$e_1 = \frac{4\pi}{3}\left(\frac{9\eta}{2}\right)^{3/2}\left(\frac{1}{g(\sigma-\rho)}\right)^{1/2}\frac{(v_1+v_2)_0 v_1^{1/2}}{F}$$

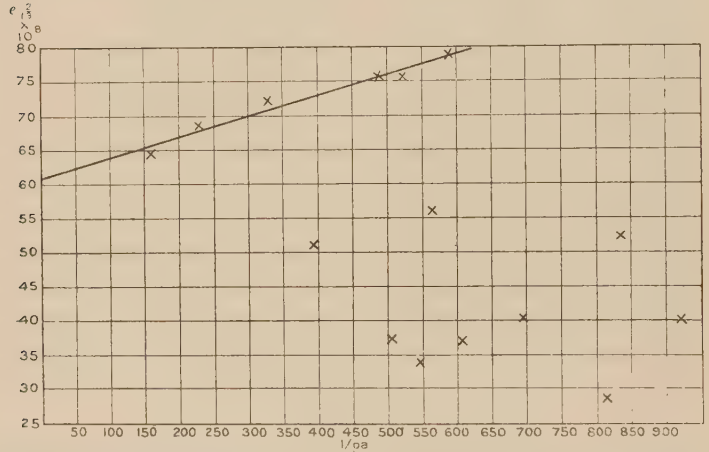
which is derived from the uncorrected form of Stokes's law. Then $e_1^{2/3}$ was plotted against $1/pa$ in the familiar Millikan‡ method. Fig. 2 shows the results obtained. The very sensitive, that is the larger, drops fall on, or close to, Millikan's line, as shown in the figure, and give the correct value for e. The slightly sensitive and insensitive drops—these coincide with those which fall very slowly, and hence for which a is apparently small—give low values for e, and show no regularity in respect to position on the graph. In order to bring them upon Millikan's line, it is necessary to assume for all these irregular drops densities much lower than that of mercury—in the cases of some of them a density as low as one-ninth that of mercury. These are the droplets that Wasser assumes are pure mercury, although their densities are hereby shown

* Wasser, *Zeit. f. Phys.* Bd. xxvii. Heft 4, p. 207 (1925).
† Millikan, Phys. Rev. xxii. (1923).
‡ Millikan, 'The Electron,' pp. 91, 105.

to be as low as 1·5. Evidently he is working with an airy cluster of some kind.

This conclusion has recently been arrived at in Vienna itself by Mattauch, Ehrenhaft's assistant, who has determined the densities of these slowly falling droplets, obtained by condensing mercury. He has determined these densities by measuring the rate of fall of the same particle at two or more different pressures in nitrogen, and has thus been able to make his computations independent of any use whatever of the charges carried by the drops. He, like myself, finds the densities of the most slowly falling of his drops to be

Fig. 2.



between 1 and 2, instead of 13·6. *These results, added to my own proof of the insensitivity of these drops to ultra-violet light, of course show definitely that these slowly falling particles are not solid spheres of mercury.* The precautions which both Wasser and I have taken to obtain pure mercury are really of no significance for these experiments: first, because chemical methods of purifying mean nothing when such minute quantities of oxides or other impurities as are required to coat a few sub-microscopic particles are concerned: and second, because, even if perfectly pure mercury be assumed, there is nothing at all to show that pure mercury may not in the process of condensing sometimes form into clusters of particles so small that they might be insensitive to light of longer wave-length than 1800 Å., such as Wasser and I have used. As Millikan has recently pointed out, the gaseous molecules of mercury have a long wave-length limit of about 1200 Å., while liquid mercury has its long wave-length limit

at 2735 Å. How large the aggregate must be before the latter limit is reached, no one knows.

My results agree with Wasser's in that the points in fig. 2 may be divided into three regions: in the first of these the drops show only normal effects in ultra-violet light; in the second region some drops are sensitive in ultra-violet light and others are not, or only slightly so; in the third region all drops are insensitive. We agree, also, in that the slightly sensitive or insensitive drops are the ones that yield apparent values of "e" less than $4{\cdot}77 \times 10^{-10}$ E.S.U.

VI. *Value of the Constant* A *for* Hg.

The line drawn through those six points in fig. 2, which, from data on their behaviour in ultra-violet light, we conclude to be pure mercury, gives $e = 4{\cdot}77 \times 10^{-10}$. The value of the correction constant A in Stokes's law when calculated from the slope of this line is ·695, a value in very good agreement with that obtained by Derieux *. This is of theoretical interest, as Millikan † has shown that in the generalized law of fall ·7 is the lowest value that A can have, and corresponds to the case of diffuse reflexion of gas molecules from the surface of the drop. It is also the lowest value that has ever been obtained for any material or that theoretically can be obtained.

VII. *Summary.*

The inverse photo-electric effect is a spurious effect, and is not due to discharge of positive electricity. This has been proved by careful work on oil, glycerine, and mercury drops in various gases. Work with mercury drops shows that the drops that yield values of "e" smaller than $4{\cdot}77 \times 10^{-10}$ E.S.U. also show an abnormal behaviour to ultra-violet light—that is, they are only slightly sensitive or not sensitive at all.

The multiple relationship holds for the charges on these insensitive drops, proving that their charges are electronic, and that it is erroneous to assume their density to be that of mercury.

Drops that are known to be pure mercury satisfy Millikan's $e_1^{2/3}$, $1/pa$ relation, and yield $4{\cdot}77 \times 10^{-10}$ E.S.U. for the electronic charge, and ·695 as the value of the correction constant, A, in Stokes's law.

Norman Bridge Laboratory of Physics,
California Institute of Technology, Pasadena.
August 6, 1925.

* Derieux, Phys. Rev. xi. (1918).
† Millikan, *loc. cit.*

XLII. *The Solubility of Hydrogen in Tin and Aluminium at High Temperatures.* *By* L. L. Bircumshaw, *B.A., M.Sc., from the National Physical Laboratory* *.

A CONSIDERABLE amount of work has been recorded on the occlusion of gases by solid metals, chiefly the systems palladium-hydrogen and platinum-hydrogen, but, except by Sieverts and his collaborators (*Zeit. Phys. Chem.* lxviii. p. 115, 1910; lxxiv. p. 277, 1910; lxxvii. p. 591, 1911), very little attention has been paid to an examination of the solubility of gases in metals in the liquid state. In the cases investigated where solubility occurred, Sieverts found in general that solubility increases regularly with rise of temperature, very rapidly in the region of the melting-point and then again regularly with further rise of temperature. This applies to hydrogen in nickel, iron, and copper, where the solubility was determined between 400° C. and 1600° C., and up to one and a half atmospheres pressure of the gas. An extremely important result obtained is that both for the solid and liquid state at a constant temperature the solubility is proportional to the square root of the pressure, but at pressures below 100 mm. deviations from this relation were found. The direct application to this result of the van't Hoff Nernst distribution law $m = K\sqrt{P}$, where m is the mass of gas dissolved, leads to the conclusion that the gas dissolves as atoms and not as molecules. This relation has also been found to hold for the solubility of oxygen in silver by Donnan and Shaw (Jour. Soc. Chem. Ind. xxix. p. 987, 1910), who verified it for eight different pressures of the gas at 1075° C. These authors call attention to an important point: the fact that the solubility follows this relation does not allow us to distinguish between the possibility of solution as oxygen atoms or as silver monoxide. Sieverts and Krumbahr (*loc. cit.*) found that for sulphur dioxide in liquid copper $m = k\sqrt{P}$, and considered it very surprising that the law was followed in this case. They pointed out the possibility of this law being characteristic for all metallic solutions of gases and that the usual explanation (*i.e.*, that the gas dissolves as atoms) may be incorrect. Stubbs, who studied the solubility of this gas in copper by observations of the depression of the freezing-point (J. Chem. Soc. lxxiv. p. 1445, 1913), explains his results as being due to the *partial* formation of oxide and sulphide

* Communicated by the Director.

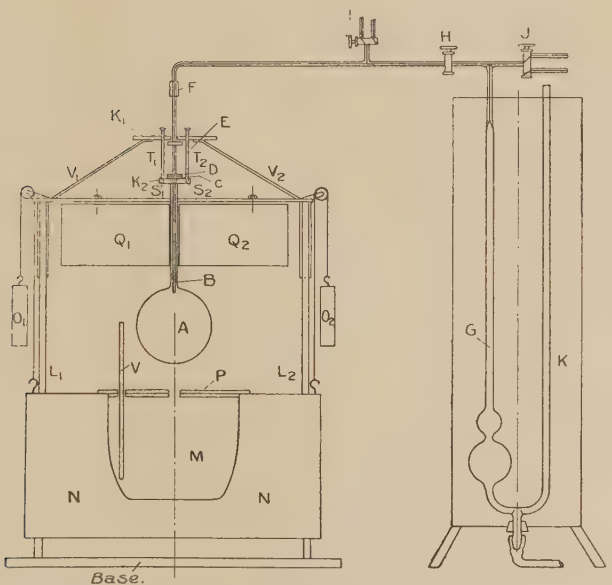
according to the following equation: $6Cu + SO_2 = Cu_2S + 2Cu_2O$. Sieverts found that hydrogen was quite insoluble in cadmium, thallium, zinc, lead, bismuth, tin, antimony, silver, gold, and aluminium, and that in the majority of cases where solubility occurred equilibrium was instantaneous.

The present work was undertaken with a view to investigating the absorption of different gases by a number of metals, especially aluminium, and it was first decided to verify Sieverts's observation on hydrogen and one of the metals of low melting-point—*e. g.*, tin.

Experimental.

A diagram of the apparatus is shown in fig. 1. A is a

Fig. 1.



vitreous silica flask (capacity 100 c.c.) with a long neck terminating in a collar C, whose upper surface is ground flat. Into the neck of this flask fits the silica capillary rod B which carries two collars—D, whose lower surface has been ground to fit C, and another at E. B is fitted closely, by means of a short piece of pressure-tubing at F, to a capillary glass tube which connects the apparatus with a gas burette. The burette has a total capacity of 48·75 c.c. and is graduated with an arbitrary scale whose large divisions are equal to

0·6 c.c. approximately, and are divided into tenths. The burette was calibrated in the Metrology Department of the N.P.L., and by using a telescope 1/10 of a small division could be estimated. A two-way tap was fused in at H, a three-way tap at I made connexion to a pump and a McLeod gauge and served to fill the apparatus with air when necessary. Another three-way tap was fused on to the other side of the burette (which was contained in the water-jacket K). This tap served to fill the apparatus with gas. The flask was held in position between the metal rings K_1, K_2, a thin rubber washer being interposed between each ring and the collar of the rod, C and D were held together with the necessary tightness by means of the screws (S_1, S_2, S_3) in the connecting rods (T_1, T_2, T_3). The ring K_1 was firmly attached to the vertical supports of the furnace by the steel strips (V_1, V_2, V_3). The heating was conducted in a bath of molten tin M contained in a salamander pot wound with nichrome wire and heated electrically. The pot, lagged with magnesia packing, was fixed into the furnace box N, which contained three iron tubes through which fitted loosely the supports L_1, L_2, L_3. By means of the counter weights (O_1, O_2), N could be drawn up and fixed in any position. When the flask was immersed in the metal bath, two copper water-coolers (Q_1, Q_2), shaped to fit closely round the neck of the flask, rested on the "Mabor" plate P which covered the pot. Good metallic contact between the coolers and the neck of the flask was made with thin copper-foil. The silica thermocouple tube V passed through a narrow tube in one of the coolers, so adjusted as to fit exactly over a small hole in the "Mabor" plate. Nitrogen was passed slowly above the surface of the metal through a similar tube in the other cooler to prevent the rapid oxidation of the tin which otherwise occurred. When the flask was in the bath it was immersed to a point above the beginning of the narrow neck. Before each experiment was commenced, the level of molten tin in the pot was adjusted accurately by means of a steel point suspended from a horizontal steel grip placed flat on the horizontal top of the furnace. The ground joint D–C and the joint at F were made gas-tight by means of a little sealing-wax varnish, and water was passed through the coolers from a constant head to ensure a constant temperature gradient between the bulb and the neck.

The principle of the method employed was extremely simple. The volume of gas required to fill the flask at any given temperature was determined. A known weight of metal was then introduced and the volume of gas required to fill the flask again determined. From these data and the density of the metal at that temperature the volume of gas

absorbed was calculated, for if V_c is the calibration volume of the flask, V_D the volume required to fill the flask when containing the metal, and V_M the volume of metal at that particular temperature (all volumes being, of course, reduced to 0° C.), then the volume of gas absorbed is $(V_D + V_M) - V_c$. The hydrogen used was prepared by the electrolysis of 5 per cent. sodium hydroxide solution, and was freed from traces of oxygen by passing the gas over silica chips at 500° C. and afterwards drying.

The calibration was made in the following manner: After the flask had been immersed in the furnace for some time and a constant temperature attained, the flask and capillary up to the tap H were exhausted through I. The burette was filled with gas by lowering the mercury until it just sealed the junction between the burette and levelling tube. Hydrogen was then bubbled through from J for half an hour, when the latter was turned and the mercury levelled. One operator then carefully opened the tap H, allowing the gas to flow over into the evacuated flask, while another gradually raised the mercury in the burette. The mercury was then levelled and read, and the temperature of the water-jacket noted. It was found that the volume determined in this way could be repeated usually to 0·05 c.c., and the tightness of the apparatus was tested by allowing the gas to remain in the flask for some time when no alteration of the level of the mercury could be detected. In some cases this was continued for two hours. The whole process was then repeated with a known weight of metal in the flask.

Tin-Hydrogen.

Experiments were first made at 306° C. The metal used contained 0·13 per cent. of impurities which consisted of As 0·04 per cent., Pb 0·02 per cent., Cu 0·02 per cent., Fe 0·01 per cent., Ni 0·02 per cent., Zn 0·02 per cent. It was just melted, skimmed, and poured into the weighed flask. The metal in the flask weighed 579·1 grams. It was heated *in vacuo*, pumping being continued all the time, and allowed to cool, this treatment being repeated the next day. Hydrogen (purified and dry) was then admitted in the manner described above. The time and burette readings are given below:—

Time	Burette-reading.	Temperature of water-jacket.
3.9	31·54	18·0° C.
3.14	31·54	„
3.30	31·52	„
4.0	31·50	„
5.15	31·50	18·1

The division 31·50 on the burette corresponds with a reading of 20·60 c.c., the initial volume of gas 28·72 c.c., $V_D = 7{\cdot}68$ c.c. The calibration volume of the flask was 53 85 c.c., and the reduced volume occupied by the metal was 46·25. The density of tin at 306° C. was taken as 6·96, the mean of the values given by Pascal and Jouniaux (*Comptes Rendus*, clviii. p. 415, 1914) and Day and Sosman (Amer. J. Science, p. 10, 1914), so we have

$$(V_D + V_M) - V_C = 0{\cdot}07 \text{ c.c.}$$

In another experiment made in another flask at the same temperature 723·7 grams of metal were used. Initial volume of gas in burette 28·72 c.c.:—

Time.	Burette-reading.	Temperature of water-jacket.
2.42	34·10	18·0° C.
4.42	34·00	18·8°

34·00 corresponds with a volume of 22·09 c.c. so that $V_D = 6{\cdot}22$ c.c., $V_M = 49{\cdot}21$ c.c., and V_C in this case 55·38 c.c., hence $V_D + V_M - V_C = 0{\cdot}05$ c.c. Both of these results are well within the possible error of a determination, so it was concluded that the solubility of hydrogen in tin at this temperature is extremely small.

Experiments were next made at a temperature of 800° C. The weight of metal taken was 437·9 grams, and it was heated at 800° C. *in vacuo* for about 12 hours, which included 2 hours at 800° C. Hydrogen was then introduced and the rate of absorption of gas is given in the following table:—

Time.	Burette-reading.	Temperature of water-jacket.
2.20	18·81	20·9° C.
2.35	18·20	21·0
2.45	17·91	21·1
3.0	17·60	21·3
3.30	17·15	21·7
4.10	16·70	22·2
5.10	16·30	22·7
6.10	16·05	22·9

Mean Barometer: 747·7 mm.

The final reading in the burette 16·05 corrected to the initial temperature 20·9° C. corresponds with a volume V_D of 16·02 c.c., and the corrected volume of the metal is 16·83 c.c. The mean calibration value of the flask was 31·31 c.c., so that the gas dissolved was 1·51 c.c. (N.T.P.). The density of tin at 800° C. was taken as 6·62. the mean between the value

given by Day and Sosman (Amer. J. Science, p. 10, 1914) and Bornemann and Sauerwald (*Zeit. f. Metallkunde,* xiv. p. 145, 1922).

The metal from the previous experiment was heated *in vacuo* for about 12 hours (including two hours at 800° C.) and hydrogen introduced again :—

Time.	Burette-reading.	Temperature of water-jacket.
12.50	19·00	18·8° C.
1.2	18·52	19·0
1.17	18·20	19·1
2.5	17·90	19·6
2.30	17·60	19·9
3.0	17·50	20·0
3.45	17·31	20·3
4.15	17·20	20·8
4.45	17·10	21·0

Mean Barometer: 763·3 mm.

Here V_D is 15·58 c.c., so that the gas dissolved is 1·10 c.c. (N.T.P.).

The metal was again subjected to the same treatment, heating *in vacuo* for about 12 hours including two hours at 800° C., and hydrogen introduced once more :—

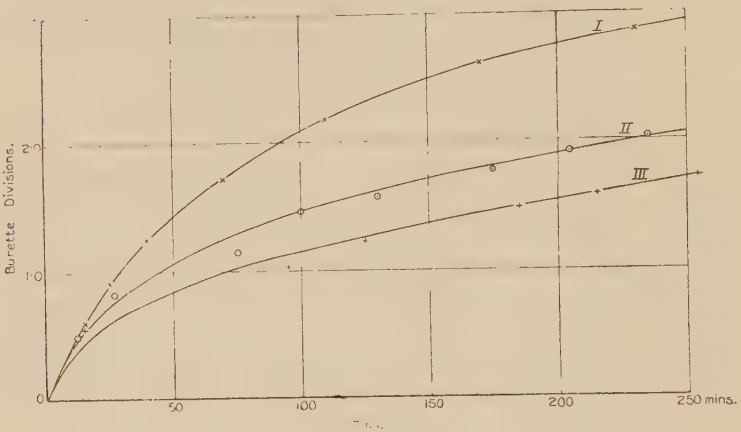
Time.	Burette-reading.	Temperature of water-jacket.
12.45	18·52	22·0° C.
1.2	18·00	22·4
2.20	17·60	23·8
2.50	17·40	24·2
3.50	17·20	25·0
4.20	17·11	25·1
5.0	17·00	25·4

V_D is 15·50 c.c. and the gas dissolved is 1·01 c.c. N.T.P. These experiments were continued until the absorption was of the order of one-tenth of a c.c. per hour, and the results are shown graphically in fig. 2. It is practically certain that the point 0 is not the true origin for curves II. and III., *i. e.*, the time of heating after experiment 1 was insufficient to remove all the gas from the metal. It will be seen that saturation has not been reached.

Adeney and Becker (Scient. Proc. Roy. Soc. Dub. xv. p. 385) in an investigation on the rate of solution of several gases in water and salt solution found the relation $w=\frac{a}{b}-ce^{-bt}$, where w is the amount of gas dissolved at time t and a, b, and c are constants. From this it follows that

dw/dt plotted against w should be a straight line. This formula is developed on the assumption that the liquid is well stirred, *i. e.*, at any moment there are no concentration gradients of gas in the liquid. It was conceivable that there might be sufficient convection in the molten metal to approximate to this relation. The tangent-derived curve from I. (fig. 2), plotted against w, is shown in fig. 3, and it will be seen that a well-marked curve is obtained.

Fig. 2.



There is the possibility that the process is governed by the diffusion of the gas through the metal. In this case the rate of absorption should be determined by Ficks's well-known law,

$$\frac{\partial w}{\partial t} = k\left(\frac{\partial^2 w}{\partial x^2} + \frac{\partial^2 w}{\partial y^2} + \frac{\partial^2 w}{\partial z^2}\right).$$

If we assume that diffusion takes place from an infinitely thin saturated layer on the surface the problem approximates to the case cited by Mellor (Higher Mathematics, p. 489, problem 5), in which a cylinder containing a saturated salt solution is immersed in pure water, and we may assume that the solution will be of the same form except that the constants will be chosen to satisfy the new boundary condition, viz. :

$$\text{when } x=0, \quad w=w_0 \text{ a constant},$$

$$\text{when } r=a, \quad \frac{\partial w}{\partial r}=0,$$

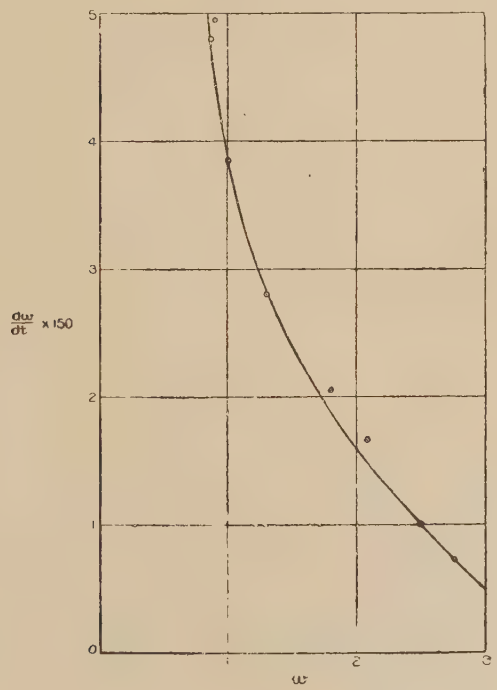
for all values of t. If w is the volume of gas dissolved, the equation will be of the form

$$w = A + Be^{-\alpha t} + Ce^{-9\alpha t} + \ldots,$$

where A, B, C, and α are constants. If we neglect the last term on the right-hand side of this equation, differentiate w with regard to t, and substitute for B, we get

$$\frac{\partial w}{\partial t} = -\alpha(w - A).$$

Fig. 3.



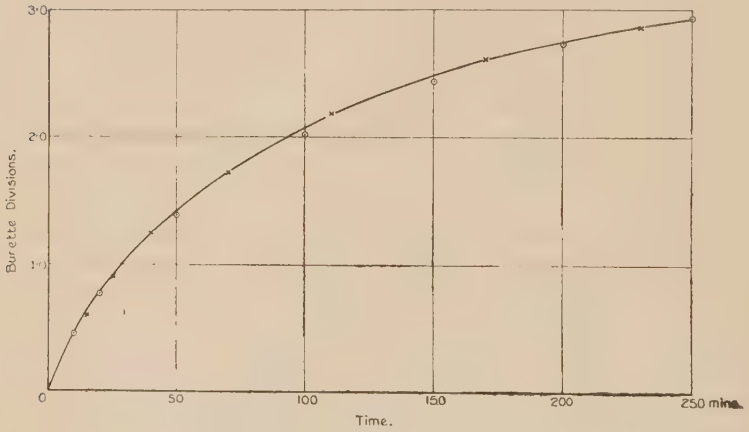
A value for α is obtained in this way from the lower part of the curve shown in fig. 3, where the term $Ce^{-9\alpha t}$ is negligible. The final equation assumes this form

$$w = 3{\cdot}38 - 2{\cdot}86e^{-{\cdot}0074t} - 0{\cdot}52e^{-{\cdot}0666t}.$$

In fig. 4 the curve I. from fig. 2 is reproduced and the points ⊙ are values calculated from the above equation. When t is infinite $w=3\,38$, and this is the saturation value and corresponds with a solubility of 4·19 c.c. N.T.P. per kilogram of metal.

Since the completion of the above work a paper has appeared on the solubility of oxygen in silver (N. Parravano and G. Malquori, Atti R. Acad. vi. 1, p. 417, 1925). These authors come to the conclusion that the velocity of absorption of the gas is a function of the velocity with which the gas diffuses into the interior of the metal.

Fig. 4.



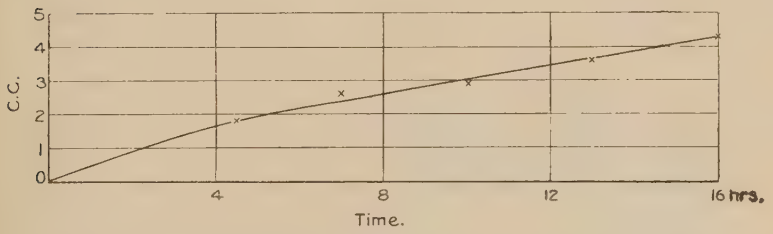
Experiments on Aluminium.

Great difficulty was experienced, owing to the attack on the silica vessel by the metal. It was found that whenever the flask was filled with molten metal the freezing of the latter always led to the breaking of the flask. An attempt was made to use a fine film of some protective coating, and the best results were obtained with a mixture which consisted of 7·5 grams of pure alumina and 7·0 grams of china-clay made into a fine cream with 25 c.c. of water. A few c.c. of this mixture were pipetted into the flask, which was rapidly rotated and gently warmed until a very fine even coating was obtained, and the flask was then heated for a time to 1100° C.

A preliminary experiment showed the metal to contain a

certain amount of gas. 125·3 grams of aluminium * were heated *in vacuo* for 109 hours at 800° C. and 19·45 c.c. of gas obtained. On analysis this gas was found to contain 82·30 per cent. of hydrogen. Carbon monoxide, carbon dioxide, and oxygen were found to be absent. Heated for another five hours a further quantity of 1·7 c.c. of gas was obtained which contained 75 per cent. of hydrogen ; the rest of the gas in these experiments appeared to be nitrogen. It was found to be almost impossible to keep the apparatus absolutely tight for such long periods of time, but tests made on the apparatus before and after the experiment showed that the total leak would account for about 0·8 c.c. of nitrogen, so that it is extremely probable that some of this gas is actually evolved on heating the metal. Guichard and Jourdain (*Comptes Rendus*, clv. p. 160, 1912) obtained from a sample of aluminium a quantity of gas which contained 10 per cent. of nitrogen.

Fig. 5



Owing to two breakdowns of the furnace it was not possible to determine the rate of evolution of the gas over the whole period of heating, but it is shown for the first sixteen hours in I (fig. 5). It will be seen that the rate of evolution is practically linear after the first four hours, but the accuracy of these observations is not very high.

At this stage it was quite obvious that there still remained a considerable quantity of gas in the metal, but, owing to the probability of the metal getting through the protective coating on the flask, it was decided to attempt to obtain a very approximate value for the solubility. Pure hydrogen was therefore introduced and the following observations were recorded. The temperature of the metal was 670° C.

* The aluminium contained 0·21 per cent. of silicon and 0·17 per cent. of iron.

Time.	Burette reading.	Temperature of water-jacket.
1.50 P.M.	10·56	19·1° C.
2.0	10·05	19·6
2.30	9·40	19·8
3.30	9·32	20·1
4.30	8·94	20·5
5.30	8·73	21·0
6.30	8·64	21·2
7.30	8·50	21·4
8.30	8·44	20·8
9.0	8·38	20·4
9.30	8·22	20·2
10.30	8·08	20·0
11.30	7·89	20·3
12.40 A.M.	7·77	21·0
2.0	7·65	22·1
3.30	7·54	22·3
5.0	7·40	21·8
6.30	7·25	21·9
8.0	7·12	22·7
9.30	7·02	23·0
10.30	6·93	22·9

Mean Barometer: 767·9 mm.

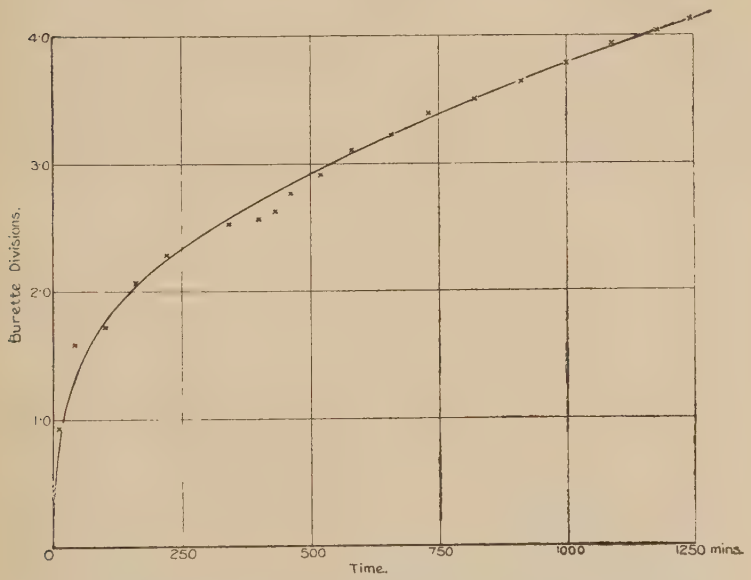
The density of aluminium at 670° C. was taken as 2·378 (Edwards and Moorman, Chem. and Met. Eng. xxiv. p. 61, 1921), and calculation showed that before the first reading was taken, 0·24 c.c. of gas had entered the metal. This corresponds with 0·40 burette-divisions. These results (corrected for the immediate absorption 0·4) are shown graphically in fig. 6. The rate at which gas is being absorbed at the end of the experiment is of the order of 0·05 c.c. per hour; nevertheless, it is readily seen from the curve that even after this time (20 hours) the metal is apparently far from saturated. The final measurement (at 10·30 A.M.) corresponds with a solubility of 18·67 c.c. (N.T.P.) per kilogram.

The metal was frozen in hydrogen and cooled, the residual gas pumped off cold, and the metal once more heated to 670° C. for a period of 20 hours. 2·36 c.c. of gas were obtained, which analysis showed to contain 2·0 c.c. of hydrogen. The amount of gas which in the previous experiment had been absorbed during this time was 2·34 c.c. In this case, then, practically the same amount of gas which is absorbed in a certain time is given off on heating *in vacuo* for the same time, but it is extremely probable that in this case we are dealing with a relatively thin layer of the metal.

One important point which arises from these experiments

is the very long duration of heating *in vacuo* which appears to be necessary to expel the dissolved gas from a metal In the case of aluminium mentioned above, after 114 hours gas was still coming off. If we consider the formation of a spherical bubble of radius r in the interior of a metal of density ρ at a depth h cm. below the surface, then, if T is the surface-tension of the metal, a pressure $\left(h\rho g + \frac{2T}{r}\right)$

Fig. 6.



dynes/cm.^{2} must be exceeded in the bubble before it can grow. When the bubbles are very small, of course, the term $\frac{2T}{r}$ becomes considerable, and for a minute bubble forming in a metal its value may be from five to ten times greater than in the case of a bubble of the same size forming in water. The suggestion is put forward that the difficulty of removing the gas dissolved in a metal is due to the relatively high surface-tension of the medium in which the gas bubbles are formed.

W. C. McC. Lewis (Journ. Chem. Soc. cxvii. p. 623, 1920) has put forward the theory that the ability of a metal to dissolve gas depends on the ability of the metal to dissociate the gas, and he calculates the critical increment of dissociation per gram mol. of hydrogen in the case of a number of metals.

For pure hydrogen in contact with a metal we have from mass-action considerations $k_1 = \frac{[H]^2}{[H_2]}$ in the gas phase, and also a further equilibrium $k_2 = \frac{[H]}{[H_M]}$ between the atomic hydrogen in the gas phase and the metal. Presumably hydrogen is dissociated in the surface-layer, and diffusion of the atoms takes place until their concentration in the metal is uniform. On these assumptions the most probable mechanism of the removal of gas in the absence of nuclei and bubble formation would be the diffusion of the atoms to the surface where re-combination into molecules takes place. In this case the rate of absorption of gas by a metal should be equal to the rate of evolution when the metal is heated at the same temperature *in vacuo*.

An apparatus for the investigation of the solubilities of gases in metals has now been designed and constructed in which the gas can be bubbled through the molten metal, and further experiments are now being made.

Summary.

It appears to be practically impossible to saturate a metal with a gas by keeping the unstirred metal at constant temperature in contact with the gas, owing to the long time necessary for the attainment of equilibrium.

The statement of Sieverts that hydrogen is insoluble in tin and aluminium has not been verified. A small but definite solubility of hydrogen in tin at 800° C. has been measured, and evidence of a considerable solubility of hydrogen in aluminium just above its melting-point has been found.

The rate of solution of hydrogen in tin is determined by the rate of diffusion of gas through the bulk of the metal.

Very long times appear to be necessary to remove all the gas from a metal by heating *in vacuo*, and suggestions are made to explain this fact.

The author would like to thank Dr. W. Rosenhain, F.R.S., for his interest and advice during the progress of this work; Mr. L. F. G. Simmons, B.A., for assistance in obtaining the equation to the curve I (fig. 2), and Mr. J. Trotter for assistance in the experimental part of the work.

XLIII. *Energy in the Earth's Atmosphere.*

By D. Brunt, *M.A., B.Sc.**

1. *The Kinetic Energy of the Atmosphere* †.

If we take the parallels of 30° North and South as separating the main Easterly and Westerly circulations of the atmosphere, the Easterly belt, covering a range of 60° in latitude, will contain half the mass of the atmosphere. Assuming the average pressure to be one atmosphere, we can readily deduce an approximate value of $2{\cdot}7\ 10^{21}$ grammes, or $2{\cdot}7\ 10^{15}$ metric tons. Taking the mean velocity to be 10 metres/second, a value which is in agreement with the distribution of pressure, we find the kinetic energy of the equatorial belt to be

$$\tfrac{1}{2}\ 2{\cdot}7\ 10^{21} \times 10^{6}\ \text{ergs} = 1{\cdot}35\ 10^{27}\ \text{ergs}$$

The combined masses of the polar caps will not differ appreciably from the mass of the equatorial belt, and the moment of momentum of the two circulations should balance, since they are produced by internal reactions within the earth's atmosphere. The equality of moments of momentum demands that the Westerly velocity should be the greater, and the energy of the combined polar caps should exceed somewhat that of the equatorial belt.

It appears safe to assume that the total kinetic energy of the earth's atmosphere is of the order of $3\ 10^{27}$ ergs.

This estimate does not specifically include the energy of the circulations around cyclones and anticyclones An estimate has been given by Sir Napier Shaw of the kinetic energy of a cyclone which formed over the lower part of the North Sea between July 27th and August 3rd, 1917, which incidentally ruined an allied offensive movement in Flanders. This depression was apparently formed *in situ*, and filled up *in situ*. Its diameter was about 1400 km. and the depth at the centre was 10 millibars. The kinetic energy developed was $1{\cdot}5\ 10^{24}$ ergs.

If the kinetic energy of the earth's atmosphere, roughly computed above, were spread uniformly over the earth's

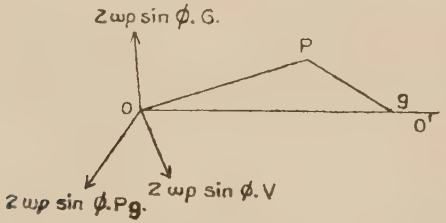
* Communicated by the Director of the Meteorological Office, Air Ministry. This paper is a slight expansion of a paper communicated to the British Association in 1923.

† This section follows the lines of a discussion by Sir Napier Shaw in the 'Dictionary of Applied Physics,' vol. iii. p. 67.

surface, the amount contained in the portion of the atmosphere over a circle of diameter 1400 km. would be 10^{24} ergs, so that in the case considered the kinetic energy of the cyclone was about 50 per cent. higher than the average kinetic energy of the general circulation.

2. *The Dissipation of Energy by Turbulence.*

The kinetic energy of the atmosphere is subject to a continual dissipation due to the effect of turbulence. It is proposed to estimate the amount of this dissipation. The notation used by the present writer in a paper on "Internal Friction in the Earth's Atmosphere" * will be used. Consider the conditions holding at a point O at a height z. Let OO′ be the tangent to the isobar, and let Og denote the



velocity of the geostrophic wind G. Let OP denote the actual wind, of velocity V. The diagram is drawn in a horizontal plane.

Consider now the forces acting on an element of air at O. It is acted upon by

(*a*) The pressure gradient of magnitude $2\omega\rho \sin\phi$. G, acting in a direction perpendicular to Og ;

(*b*) The "deviating force" due to the earth's rotation, of magnitude $2\omega\rho \sin\phi$. V, acting at right angles to OP. Here ϕ is the latitude, and ω the angular velocity of the earth ; and

(*c*) The effect of turbulence in producing a loss or gain of momentum. This effect may be assimilated to a viscous force, and is the "internal friction" of Ekman. Let the magnitude of this force be R.

If the motion is steady the three factors (*a*), (*b*), and (*c*) must balance. It follows then, from the triangle of forces, that R must be of magnitude $2\omega\rho \sin\phi \times Pg$, and must act in a direction at right angles to Pg.

* Q. J. Roy. Met. Soc. April 1920.

The rate at which work is done by the force R is equal to the product of R and the component of velocity along the direction of R ($\perp^r$ to gP). This amounts to

$$\begin{aligned} \mathrm{OP}\sin \mathrm{OP}g \times \mathrm{R} &= 2\omega\rho \sin\phi\ \mathrm{P}g \times \mathrm{OP}\sin \mathrm{OP}g \\ &= 4\omega\rho \sin\phi \times \text{area of triangle } \mathrm{O}g\mathrm{P} \\ &= 2\omega\rho \sin\phi \mathrm{O}g \times \mathrm{OP}\sin \mathrm{PO}g \\ &= 2\omega\rho \sin\phi \mathrm{G} \times \mathrm{OP}\sin \mathrm{PO}g. \end{aligned}$$

If we take the axis of x along OO′, the axis of y perpendicular to this, and let u and v be the component velocities along the axes of x and y, then the rate of dissipation of energy $= -v\dfrac{\partial p}{\partial y}$.

When the steady motion is along the isobar, or $v=0$, there is no dissipation of energy. If the motion is across the isobars into the low pressure, there is a dissipation of energy, and steady motion can only be maintained by supplying energy at a rate equal to the product of velocity of inflow and gradient of pressure.

The total dissipation of energy of the main current in a vertical cylinder of unit cross-section extending from the ground to the top of the atmosphere is

$$-\int_0^\infty v\frac{\partial p}{\partial y}dz.$$

This expression can be integrated if the distribution of velocity and of pressure is known at all heights.

G. I. Taylor deduced the law of variation of wind with height in the atmosphere in the case where the coefficient of eddy diffusion K remains constant at all heights. In the diagram let Og denote the geostrophic wind in magnitude and direction, let OP or V denote the wind at height z above the ground *, and let α be the angle between the direction of the surface wind and the isobar. Then if we introduce a new constant B, defined by

$$\mathrm{B}^2 = \omega \sin\phi/\mathrm{K},$$

where ω is the angular velocity of the earth, and ϕ the latitude, we may write the relation between V and the height z in the form

$$\mathrm{V} = \mathrm{G} + \sqrt{2}\,\mathrm{G}\sin\alpha e^{-\mathrm{B}z+i(3\pi/4+\alpha-\mathrm{B}z)}.$$

* *i. e.* $\mathrm{V}=u+iv$.

The geostrophic wind G is assumed to be constant in the deduction of this equation. Both G and the density ρ will be treated as constant in what follows. We then have

$$\begin{aligned}-v\frac{\partial p}{\partial y} &= v \times 2\omega\rho \sin\phi \,.\, \mathrm{G} \\ &= \text{imaginary part of } \mathrm{V} \times 2\omega\rho \sin\phi \,.\, \mathrm{G} \\ &= \text{imaginary part of} \\ &\qquad 2\sqrt{2}\,\omega\rho \sin\phi \sin\alpha \mathrm{G}^2 \int_0^z e^{-\mathrm{B}z + i(3\pi/4 + \alpha - \mathrm{B}z)}\, dz \\ &= 2\omega\rho \sin\phi \sin\alpha \frac{\mathrm{G}^2}{\mathrm{B}} \left[e^{-\mathrm{B}z} \cos(\alpha - \mathrm{B}z) \right]_0^z .\end{aligned}$$

The total loss of energy in the column extending from the ground to the top of the atmosphere, assuming the same law of distribution of wind to hold, would be

$$2\omega\rho \sin\phi \sin\alpha \cos\alpha \, \mathrm{G}^2/\mathrm{B}.$$

The total loss from the ground up to the height at which the wind direction attains the direction of the tangent to the isobar, a height defined by $\mathrm{B}z = 3\pi/4 + \alpha$, is

$$2\omega\rho \sin\phi \sin\alpha \frac{\mathrm{G}^2}{\mathrm{B}} \left\{ \cos\alpha - \frac{1}{\sqrt{2}} e^{-(3\pi/4 + \alpha)} \right\} .$$

The second term inside the bracket is small by comparison with the first, so that the loss of energy up to the height

$$z = (3\pi/4 + \alpha)/\mathrm{B}$$

is approximately

$$2\omega\rho \sin\phi \sin\alpha \cos\alpha \, \mathrm{G}^2/\mathrm{B},$$

which is the total loss in the whole column extending to the top of the atmosphere. Thus with the assumed wind distribution the dissipation of energy by turbulence is effectively restricted to the layer below that at which the wind direction first attains the direction of the tangent to the isobar.

As a very rough estimate of the total amount of energy contained within this layer, we may take

$$\tfrac{1}{2}\rho \mathrm{G}^2(3\pi/4 + \alpha)/\mathrm{B}, \quad \text{or even} \quad \tfrac{1}{2}\rho \mathrm{G}^2\pi/\mathrm{B},$$

with a sufficient degree of accuracy.

The fraction of energy lost per second

$$= 4\omega \sin\phi \sin\alpha \cos\alpha/\pi.$$

The fraction of energy lost per day

$$= 4 \sin\phi \sin 2\alpha.$$

If we take

$$\sin\phi = 0{\cdot}6, \quad \alpha = 22\tfrac{1}{2}^\circ, \quad \text{or} \quad \sin 2\alpha = \frac{1}{\sqrt{2}},$$

then $$4\sin\phi\sin 2\alpha = 1{\cdot}68,$$

so that if the loss of energy were maintained at the same rate, the kinetic energy of the main current in the layer we are considering would be destroyed in a little over 14 hours.

In order to obtain some idea of the actual amount of kinetic energy destroyed by turbulence in a given time, we shall assume

$$G = 15 \text{ metres/sec.}, \quad \alpha = 22\tfrac{1}{2}^\circ, \quad B = 3\,10^{-5},$$

corresponding to

$$K = 5\,10^4, \quad \sin\phi = 0{\cdot}6, \quad \text{and} \quad \rho = 1{\cdot}2\,10^{-3} \text{ grams/cm.}^3$$

Then the rate of loss of kinetic energy in the column disturbed by turbulence due to the ground

$$= 2\omega\rho\sin\phi\,G^2\sin\alpha\cos\alpha/B$$
$$= 3\,10^3 \text{ ergs sec./cm.}^2$$
$$= 3\,10^{-3} \text{ kilowatts/(metre)}^2.$$

With the wind distribution assumed above, the loss of kinetic energy through turbulence becomes negligible above the height at which the gradient wind direction is first attained. This height is given by

$$z = (3\pi/4 + \alpha)/B,$$

and if B be assumed to be $3\,10^{-5}$ this height is about 1 kilometre.

At greater heights, the changes of wind with height are determined, not by turbulence produced at the ground, but by the horizontal distribution of temperature. An examination of recorded wind distribution is necessary.

The rate of loss of energy

$$= K\rho\left\{u\frac{\partial^2 u}{\partial z^2} + v\frac{\partial^2 v}{\partial z^2}\right\},$$

or in terms of finite differences

$$= K\rho\left\{u\frac{\Delta}{\Delta z}\cdot\frac{\Delta u}{\Delta z} + v\frac{\Delta}{\Delta z}\frac{\Delta v}{\Delta z}\right\}.$$

A number of sample cases when conditions were relatively steady were worked out, showing that at 3 km. the term

$$u\frac{\partial^2 u}{\partial z^2}+v\frac{\partial^2 v}{\partial z^2}$$

is of the order of $2\ 10^{-4}$ to $3\ 10^{-4}$, while at 10 km. it is of the order of $\frac{1}{2}\ 10^{-4}$ to $1\ 10^{-4}$. We shall therefore assume, as a rough average value from 1 to 10 km., that

$$u\frac{\partial^2 u}{\partial z^2}+v\frac{\partial^2 v}{\partial z^2}=2\ 10^{-4}.$$

At the ground $K\rho = 5\ 10^4 \times 1{\cdot}3\ 10^{-3} = 65.$

At 5 km. $K\rho = 5\ 10^3 \times 7\ 10^{-4} = 3{\cdot}5.$

$K\rho$ thus decreases rapidly with height in the troposphere, and the average value of

$$K\rho\left(u\frac{\partial^2 u}{\partial z^2}+v\frac{\partial^2 v}{\partial z^2}\right)$$

is of the order of $2\ 10^{-3}$ ergs per sec. per cm.^{3}

$= 18\ 10^6$ ergs per sec. per metre^2 of the earth's surface,

$= 1{\cdot}8\ 10^{-3}$ kilowatts per metre^2.

Above 10 kilometres the value of

$$u\frac{\partial^2 u}{\partial z^2}+v\frac{\partial^2 v}{\partial z^2}$$

is small except at the base of the stratosphere. No data are available for the estimation of the dissipation of energy at this level, but no very considerable error can arise if we neglect the dissipation above 10 kilometres. We then have for the dissipation above 1 square metre of the earth's surface :

From the ground to 1 km. ...	$3\ 10^{-3}$	kilowatts per metre^2.
From 1 km. to 10 km.	$2\ 10^{-3}$	" " "
Total	$5\ 10^{-3}$	" " "

This total is the rate at which the kinetic energy of the earth's atmosphere is being dissipated by turbulence. It is probably an overestimate for those regions of the earth's

atmosphere in which the winds are normally light at all heights, but so far as order of magnitude is concerned it may be accepted with a fair degree of faith, in spite of the numerous approximations made. On the whole it appears likely to be an overestimate rather than an underestimate.

The total energy above one square metre of the earth's surface, on the assumption of uniform velocity of 10 metres/sec., $= 5\ 10^{12}$ ergs. The rate of dissipation by turbulence $= 5\ 10^{7}$ ergs per metre^2 per sec. Hence, if the same rate of dissipation were maintained for 10^5 seconds, or $1\frac{1}{6}$ days, the whole kinetic energy would be destroyed in that time. If the rate of dissipation is assumed to be proportional to the total kinetic energy, then the total kinetic energy would be reduced to one-tenth its original value in three days. As no sensible change takes place in the kinetic energy of the general circulation of the atmosphere, we conclude that the loss by turbulence is being continually made up by the conversion of solar energy into kinetic energy.

The expression which gives the relation between the wind V and the height z demands that the wind should increase with height, eventually surpassing the magnitude of the geostrophic wind G, and through a considerable layer whose thickness should exceed $\frac{1}{2}$ km. the wind velocity should everywhere exceed the geostrophic wind G. If the earth's surface were everywhere flat and smooth, so that no turbulence could originate at its surface, we should expect to find the wind at all heights equal to the geostrophic wind, at any rate for straight isobars. But when the hypothetical smooth earth is replaced by the irregular surface of the earth as we know it, the wind velocity is decreased in the lowest layers, and increased in a higher layer. It is difficult to conceive of the physical mechanism which could bring this about. Is it analogous to a wheel spinning freely about a horizontal axis? In this case, when the wheel is free of all constraints at its periphery, and spins about its centre, every point is moving with the same velocity. But if the wheel is made to rotate in contact with a rough surface, the part in contact with the surface is instantaneously at rest, and the topmost point of the wheel has its velocity doubled. The difficulty of understanding the somewhat analogous motion in the atmosphere is largely due to the difficulty of drawing a mental picture of the behaviour of an individual eddy.

3. *Comparison of the Eddy-Dissipation of Kinetic Energy with the Radiation coming in from the Sun.*

The value of the solar constant being taken as 2 gramme calories per cm.^{2} per minute, then the amount of radiation coming from the sun into the earth's atmosphere

= 2 g. cal. per cm.^{2} per min. = 8·36 joules per cm.^{2} per min.

= 83600 joules per metre^2 per min.

= 1400 joules per metre^2 per sec.

= 1400 watts per metre^2.

= 1·4 kilowatts per metre^2.

But the radiation intercepted by the earth is the portion of the beam of solar radiation intercepted by an area πr^2, where r is the radius of the earth. This is spread over the whole area of the earth $4\pi r^2$, and hence the effective incoming radiation per metre^2 is one-fourth of the figure given above, and amounts to 0·35 kilowatt per metre^2.

Also Abbot and Fowle estimate that the effect of reflexion from the earth's surface and from clouds is to reduce by 37 per cent. the amount of solar radiation available for absorption and subsequent conversion into kinetic energy. The effective incoming solar radiation is therefore 0·22 kilowatts per metre^2, when averaged over the whole of the earth's surface.

The rate of dissipation by turbulence was given above as $5\ 10^{-3}$ kilowatts per metre^2, which is only a little over 2 per cent. of the effective incoming solar radiation.

Thus the conversion of a little over 2 per cent. of the incoming solar radiation into kinetic energy will suffice to make up for the dissipation by turbulence.

4. *The means of Conversion of Solar Energy into Kinetic Energy.*

No universally acceptable theory has been put forward to explain the mechanism of conversion of solar energy into kinetic energy.

Sir Napier Shaw, in his article on thermodynamics of the atmosphere in the 'Dictionary of Applied Physics,' vol. iii., gives a computation of the energy of a cycle of operations consisting in the heating of a mass of air at the equator to a sufficiently high potential temperature to enable it to

rise to a height of 15 km. above the equator, after which it drifts northward, losing heat by radiation until it is enabled to descend to the sea-surface in latitude 60° N., afterwards returning equatorwards along the earth's surface.

The entropy diagram shows that the amount of energy transformed into work = $2{\cdot}4\ 10^{11}$ ergs per kilogramme of air which performs the cycle. Thus the ascent of one kilogramme of air will, if it follows the cycle outlined above, contribute $2{\cdot}4\ 10^{11}$ ergs to the energy of the general circulation of the atmosphere. If every second there were 10^{11} kilogrammes of air ascending at the equator, and subsequently following the cycle outlined above, the amount of kinetic energy contributed to the general circulation would just suffice to replace the energy dissipated by turbulence.

This amounts to the ascent of 100 cubic kilometres of air per second, a relatively small quantity by comparison with the size of the equatorial belt along which the propelling power of solar radiation could be exerted.

There is strong evidence of the descent of cold air from the cold slopes of the mountains of Greenland, and of the Antarctic Continent, and the cycle of changes involved in these cases will in the same way yield a contribution to the kinetic energy of the general circulation. L. F. Richardson has estimated that the effect of radiation over the plateau of Greenland is to produce 10^{20} ergs per second, which is but a small fraction of the total dissipation of $2{\cdot}5\ 10^{22}$ ergs per second for the whole atmosphere. The descent of air over cold mountain slopes is thus not the most important factor in the maintenance of the circulation of the atmosphere.

The case first considered, of the ascent of air, at the equator raises a fundamental difficulty, in that the thermal stratification of the atmosphere is not favourable to the ascent or descent of air. Further, there is not a direct flow of air from the equator polewards in the upper atmosphere. But in view of the relatively small amount of air which is required to perform the cycle outlined by Sir Napier Shaw, it is only necessary to have a poleward flow of the upper air in a restricted portion of the equatorial belt in order to supply the kinetic energy required. Also the rain of the Doldrum regions affords direct evidence of the ascent of considerable quantities of humid air.

Margules put forward the view that, when cold and warm currents flow side by side, the mixture of the two layers, or the ascent of the warm air over the cold air, releases an amount of energy equal to the decrease in gravitational potential energy. It is, however, easier to conceive of the

process described by Margules giving rise to thunderstorms and linesqualls, than as contributing to the energy of the general circulation. It is not possible to give an estimate of the rate of production of kinetic energy by Margules's process.

It should be noted that all the views here considered visualize the conversion of radiant energy first into potential energy, and the subsequent conversion of the potential energy into kinetic energy.

5. *Summary.*

A rough estimate is given of the total energy of the general circulation of the atmosphere, and an approximate estimate of the rate of dissipation of this energy by turbulence is made, using G. I. Taylor's form of statement of the rate of vertical transference of momentum. It is found that the rate of dissipation of energy is such that, if it were maintained for rather less than a day and no energy were supplied from external sources, it would bring the whole atmosphere to rest; or if the rate of dissipation remained proportional to the total energy, it would reduce the total energy to one-tenth its original value in 3 days. It is further estimated that if about 2 per cent. of the incoming solar radiation were converted into kinetic energy, this amount would suffice to replace the energy taken from the general circulation by turbulence. It is pointed out that no generally acceptable theory has yet been put forward to explain the method of conversion of solar energy into kinetic energy of the general circulation.

XLIV *On the Variation of the E.M.F. of a Photoactive Cell, containing a Fluorescent Electrolyte, when the Amount of Fluorescent Material in Solution is Varied.* By William Rule, *M.Sc., Armstrong College, Newcastle-upon-Tyne* *.

Introduction.

A NUMBER of experimenters have shown that when one of the electrodes in a cell containing a fluorescent electrolyte is illuminated, the other electrode being kept in the dark, an E.M.F. is set up which varies with time. The most accurate and most recent work on this effect has been

* Communicated by Prof. G. W. Todd.

done by A. Grumbach *. He has shown that the E.M.F. developed is greatest and most easily generated in dilute solutions, whereas previous experimenters had used concentrated solutions, and while it had hitherto been contended that the E.M.F. was caused by the illumination of the electrode (the Becquerel effect), he has demonstrated that the phenomenon has not its origin at the surface of the electrode, but that it is essentially bound up with the illumination of the liquid itself.

Plotting E.M.F. against time a curve is obtained, and the present paper contains a description and theoretical discussion of certain experiments carried out to determine the variation of these E.M.F. time-curves when the amount of fluorescent material in solution is varied.

Apparatus.

A number of methods were tried to measure the E.M.F. set up, which is of the order of 50–100 millivolts.

The ordinary bridge method for determining small E.M.F.'s (as in the Crompton Potentiometer) was first used, but was early abandoned; while capable of showing the existence of an E.M.F., the precise measurement of this E.M.F. was impossible as the resistance of the cell was so great that the determining of the null point was very inaccurate. In a second method the cell was connected across a capacity and a charge thrown through a ballistic galvanometer.

$$C \times E = Q \propto \theta \propto \text{Scale reading.}$$

Thus, keeping the capacity constant, the E.M.F. is proportional to the Scale reading and could be determined by suitable calibration. This method was also discarded, as the capacity required to discharge through the galvanometer a quantity of electricity sufficient to give a measurable deflexion was so large as to seriously affect the E.M.F. of the cell; two readings taken the one immediately after the other were found to differ by about 20 per cent. This altering of the conditions of the cell also holds for the bridge method, where the determining of the true E.M.F. of the cell would be rendered impossible by polarization of the cell.

The most satisfactory method proved to be the direct measurement of the E.M.F. on a Dolezalek electrometer, and in all subsequent experiments this instrument has been used.

* A. Grumbach, *Comptes Rendus*, clxxvi. (January 1923).

Many types of cell were used in the course of trial experiments before a suitable one was evolved. Both mercury and silver were tried as electrodes but proved unsatisfactory, as in each case a discoloration was noticed on the illuminated electrode which was absent from the unilluminated electrode, indicating a photochemical reaction in the neighbourhood of the illuminated electrode.

A serious defect in the cells at first used was the presence of an initial E.M.F. when the cell was set up, due no doubt to the electrodes not being perfectly clean.

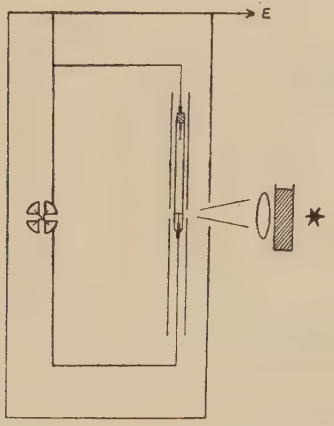
This dissymmetrical E.M.F. was, however, reduced to negligible proportions in the cell now to be described, which has been used in the experiments described in this paper. The cell, shown in fig. 1, consists of a glass tube, 20 cm.

Fig. 1.

long and 2 cm. in diameter, closed at one end, with a platinum wire electrode in the form of a flat spiral fused into the closed end and a rubber stopper, carrying a platinum wire, inserted at the other end. This cell has the advantage that the electrolyte is only in contact with the platinum and the glass, and these can be kept clean by washing out with distilled water and occasionally with chromic and nitric acids and caustic soda.

It is now convenient to describe in detail the whole apparatus shown in fig. 2. Two metal tubes are clamped in an upright position with a gap 1 cm. wide between them. The cell, round which are fixed two guides as shown, is inserted in the metal tubes so that the part of the cell where the flat spiral electrode is situated occupies the gap between the two tubes. This is the electrode which is to be illuminated. Leads are taken from each electrode to the opposite quadrants of the electrometer, the unilluminated electrode and the quadrants to which it is connected being earthed. The needle is charged permanently to 100 volts by means of a hygroscopic battery. On the glass cell, near the electrode which is to be illuminated, is affixed a paper scale,

Fig. 2.



by means of which the cell can be fixed in any desired position within the metal tubes. The whole arrangement is enclosed in an earthed metal box to shield it from external fields. A small aperture in this box allows a beam of light to pass through from outside and fall upon that part of the cell which lies within the gap between the two metal tubes. The illumination is provided by a mercury arc-lamp (240 volts, 2·5 amps.), the full radiation from which is first passed through a water-cell and then concentrated on the surface of the cell by means of a thick lens. With this apparatus the experiments described in the next section were performed.

Experimental Results.

As a solution of fluorescein and caustic soda was to be used as an electrolyte, a test experiment was first carried out using a solution of caustic soda in water (0·5 gram NaOH per 100 grams water). It was found that no E.M.F. was set up when caustic soda alone was used in solution. This simple experiment is important in so far as it shows that the E.M.F. set up in the experiments to be described presently is due to the presence of the fluorescent body fluorescein. Also it disproves a contention of Grumbach * that the action on the electrode of the fluorescent radiation emitted by the illuminated liquid is responsible for part of the E.M.F. generated in a photoactive cell such as we have described. For it is evident that in the cell containing a solution of caustic soda alone, which is much more transparent than a fluorescein solution, and which therefore allows a much more intense and fuller radiation to reach the electrode, there is more likelihood of a photoelectric E.M.F. being set up, whereas in actual fact no observable E.M.F. is generated when a pure caustic soda solution is used. It is thus seen that the essential factor in the building up of an E.M.F. is the activation of the fluorescent material in solution.

The experiments performed with varying concentrations of fluorescent material in solution will now be described.

Special precautions were taken to make up perfectly clean solutions; these were made up in the dark and stored in black flasks, the liquid being kept in the dark until the beginning of an experiment. The cell was thoroughly cleaned out after each experiment in order to prevent there being any appreciable E.M.F. present when the apparatus was set up.

In each experiment the light was concentrated fully on the electrode, which occupied a central position in the cm. gap between the metal tubes.

The concentration of caustic soda was kept constant (0·5 gram per 100 grams of water), while the concentration of fluorescein was varied (from 0·5 gram to 0·00016 gram of fluorescein per 100 c.c. of the caustic soda solution), the most concentrated solution containing about three thousand times as much dissolved fluorescent material as the most dilute solution used.

The variation of E.M.F. with time was then determined for a number of concentrations under identical conditions of illumination and disposition of apparatus. The experiments

* A. Grumbach, *Comptes Rendus*, clxxvii. (August 1923).

on a series of concentrations were repeated many times with similar results. A typical set of curves is given in figs. 3 and 4.

Fig. 3.

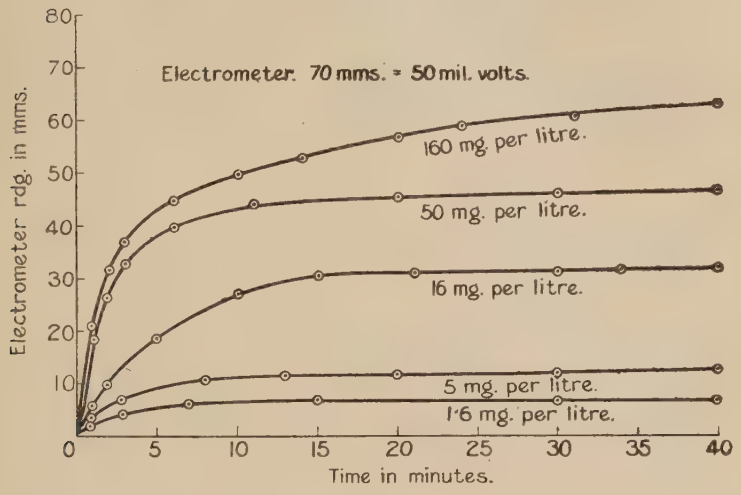
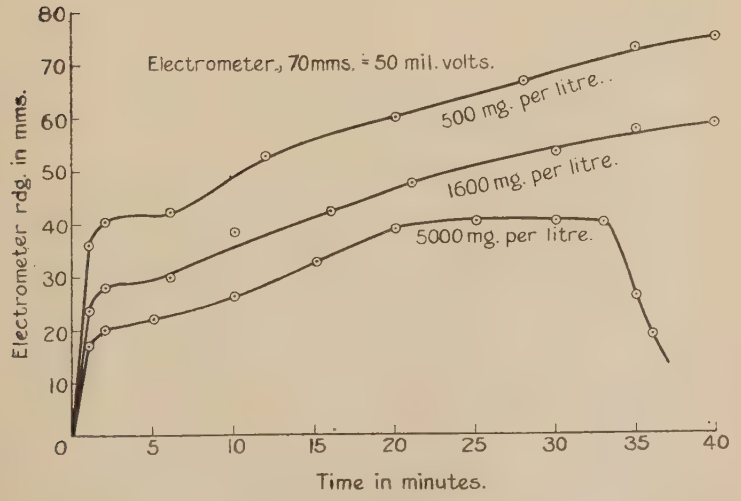


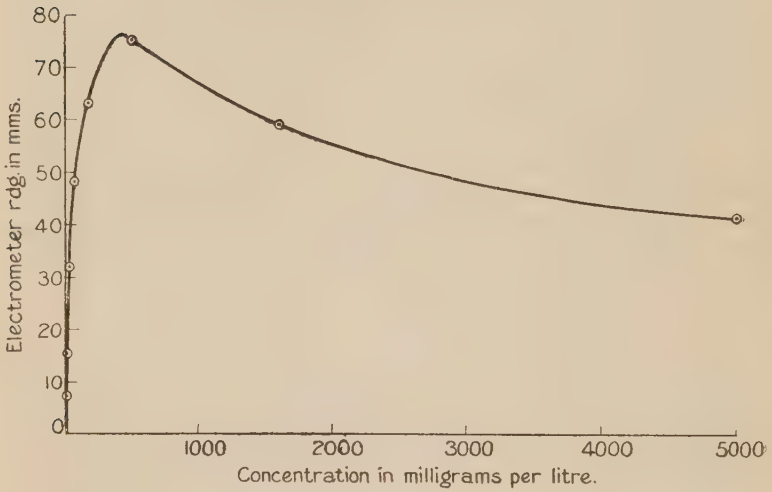
Fig. 4.



It is at once seen that while the form of the curves is similar for various concentrations of fluorescein, the magnitude of the E.M.F. generated in a given time shows a

well-marked variation. Thus for a very concentrated solution the E.M.F. set up is relatively small. As the solution becomes more dilute the E.M.F. generated in a given time increases gradually until it reaches a certain maximum, and then falls rapidly as the dilution is pushed still further. This variation is well shown in the curve given in fig. 5, where the E.M.F. attained in forty minutes (by which time it has in most cases become fairly constant) is plotted against the concentration.

Fig. 5.



The E.M.F. rises quickly to a maximum as the concentration is increased from zero, and then falls off less rapidly as the concentration is increased still further. These experiments have been repeated, using a solution of eosin in glycerine and water (10 gm. of glycerine per 100 gm. of water, and 3·0 to 0·0003 gm. of eosin to 100 c.c. of the glycerine-water solution), and show a variation in the E.M.F. attained in a given time, with concentration, similar to that which holds for fluorescein.

The E.M.F. of the illuminated electrode is negative in the case of the fluorescein solution, while in the case of the eosin solution it is slightly negative at the beginning and then takes up a much larger positive value.

Analagous Phenomena.

A.—As an E.M.F. is set up in a photoactive cell when it is illuminated, as previously described, one would expect that if suitable measurements were made a change in conductibility would be observed. Although previous experiments made with this object in view have furnished negative results, Soulan* has recently shown that this change in conductibility occurs. He gives the following results for esculine dissolved in methyl alcohol :—

N	50	20	0·01	0·005,
C	0·030	0·035	0·107	0·094,

where N is the number of milligrams of the fluorescent body dissolved per litre of solvent, and C is the limiting relative change in conductibility.

The result is interesting in that it shows the fact that the change in conductibility increases towards a maximum as the concentration decreases, and then falls off as the dilution is pushed still further.

The limiting relative change in conductibility thus varies with concentration in just the same manner as does the E.M.F. with concentration, a result one would have expected.

B.—It is known† that for the production of phosphorescence the essential factor seems to be the bringing into intimate association, in the form of a solid solution, of a small amount of active substance (the solute) and a larger amount of another substance (the solvent). The interesting fact here is that measurements of the intensity of the phosphorescence of solutions of varying concentration have shown that this intensity varies greatly with the amount of active material dissolved ; as the concentration increases from zero, the intensity of phosphorescence rises towards a well-defined maximum, and then falls off slightly less rapidly as the amount of active material is still further increased. This variation is identical with that found to hold for the E.M.F. of a photoactive cell and the concentration.

C.—J. Perrin ‡, in a recent paper, refers to the fact that fluorescent solutions are necessarily more fluorescent when they are more concentrated. He gives a curve similar to that given in fig. 5, showing that if the concentration is increased beginning at zero, the fluorescence begins to

* H. Soulan, *Comptes Rendus*, clxxviii. (March 1924).
† E. Merritt, Physical Review, v. (April 1915).
‡ J. Perrin, *Comptes Rendus*, clxxvii. (August 1923).

increase, passes through a maximum for an optimum concentration, and then decreases as the concentration is further increased. The intimate association of the E.M.F. set up in an illuminated photoactive cell containing a fluorescent electrolyte with the actual phenomenon of fluorescence is at once seen, and supports the previous contention that the effect which has been the subject of investigation is produced by the photoactivation of the fluorescent material in solution, and that its origin is not at the surface of the electrode.

Theoretical.

It has been shown that the E.M.F. developed in a photoactive cell increases rapidly from zero as the concentration is increased from zero, attains a maximum value for a certain optimum concentration, then falls off less rapidly as the concentration is increased still further. This section is devoted to an explanation of this variation on certain theoretical grounds.

The elementary phenomenon of fluorescence is as follows: A molecule M of a fluorescent body absorbs a quantum W of a certain radiation, passes to a critical state A, from which it returns to the same stable state M or another stable state M′, emitting a quantum W′ of another radiation (the fluorescent radiation). Thus:—

$$M + W \longrightarrow A \longrightarrow M(\text{or}\,M') + W'.$$

Now as the concentration, that is the number of molecules, of the fluorescent body increases from zero, the number of molecules which are activated will also increase. Therefore, assuming that the presence of these molecules in the critical state is responsible in some way for the building up of an E.M.F. in a photoactive cell, as the number of molecules activated increases with increase of concentration, so the E.M.F. will increase with increase of concentration. This explains the first portion of the curve given in fig. 5.

The experiments described, however, show that the E.M.F. does not go on increasing indefinitely, but that it attains a maximum value and then decreases as the concentration is still further increased.

This attaining of a maximum value and subsequent falling off in value of the E.M.F. indicates that, after a certain concentration, the number of molecules in the critical state requisite for the building up of an E.M.F. begins to decrease.

This decrease in the number of molecules in the requisite critical state can be explained if one adopts an hypothesis of

J. Perrin *, who assumes that in strong concentrations the molecules of the fluorescent body are "protected" by each other.

He explains the mechanism of this "protection" somewhat as follows:—As the concentration increases, the mean distance between the molecules decreases, that is, the molecules are brought into closer proximity to one another. It may be supposed that, if the molecule M, capable of absorbing a quantum of radiation, is thereby brought to a certain critical state A, it takes a certain finite time to attain its new configuration, and that it arrives there by an oscillatory phenomenon. Now if during this time a second molecule of the same nature approaches near the first, it can acquire, by resonance, part of the energy of the first and so disturb its critical state. Thus, as the concentration is increased and the mean distance between the molecules reduced, the "protective" influence of the molecules, the one over the other, increases, and so reduces the number of molecules in the requisite critical state for the building up of an E.M.F. Adopting this hypothesis, the whole of the E.M.F. concentration curve, given in fig. 5, can now be accounted for. When the solution is dilute the "protective" influence of the molecules over each other is small, and so the E.M.F. increases, as the number of activated molecules increases, with increase of concentration But as the concentration becomes greater, this "protective" influence plays a more and more important part, until the point is reached where the increase in the number of activated molecules due to the mere fact of increase in concentration is compensated for by the reduction in the number of molecules in the requisite critical state, due to the "protective" influence of the molecules over one another. As the concentration is increased still further, the "protective" influence of the molecules over each other brings about a reduction in the number of molecules in the requisite critical state, which is increasingly greater than the increase brought about by the mere fact of the concentration becoming greater.

The maximum point on the E.M.F. concentration curve, and the subsequent falling off in value of the E.M.F. as the concentration is increased, is thus explained.

I wish to acknowledge my indebtedness to Dr. G. W. Todd, of Armstrong College, at whose suggestion and under whose supervision the experiments have been carried out, and to the Department of Scientific and Industrial Research for the grant which has enabled me to undertake the work.

* J. Perrin, *Comptes Rendus*, clxxviii. (April 1924).

XLV. *Notes on the Superposition of X-Rays and on Scattering. The J Phenomenon* (Part III.). *By* Prof. C. G. Barkla, *F.R.S., and* Gladys I. Mackenzie, *M.A., B.Sc., University of Edinburgh* *.

ONE of the most remarkable features of the J phenomenon † is the evidence it affords of the divorce of the activity of an X-radiation from the wave-length of that radiation. A complex beam has an activity which is not the sum of the activities of its constituents. Such a beam has properties depending on something analogous to temperature of the radiation as a whole,—properties depending on all its constituents: this much is certain. What it indicates is (under certain conditions at any rate) the separation of quantum relationships from the frequency of radiation. It appears, indeed, that, as far as the J phenomenon is concerned, and possibly much further, there is something more fundamental than frequency; that *something* is measured by absorbability.

An experiment illustrating this and other interesting points in connexion with the scattering of X-rays and with A. H. Compton's hypothesis is briefly described below.

A primary beam is directed from an X-ray tube on to a sheet of radiating substance situated as shown in fig. 1, and the two scattered beams, proceeding in directions making angles of approximately 60° and 120° with the primary beam, are received and measured by the similar electroscopes E_2 and E_1. Absorbing sheets of the same material and equal thickness are placed at F_2 and F_1 so that the two secondary beams are intercepted in the same way. As the thickness of these absorbing sheets is gradually increased (increased by small steps), we can observe any difference in the absorbability of the radiations by finding the ratio of the ionizations produced in the electroscopes. If the two beams are exactly similar, then similar absorbing sheets should affect them similarly, and the ratio of ionizations should remain constant. Any difference in

* Communicated by the Authors.

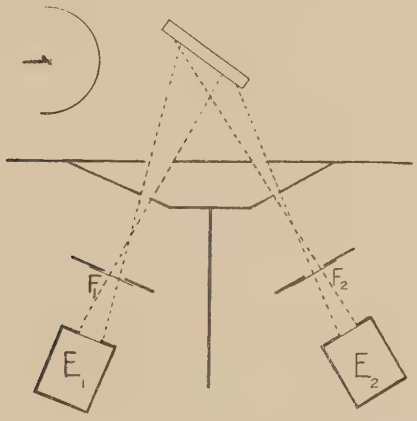
† See "The J Phenomenon in X-Rays" (Part I.), Barkla, Phil. Mag. May 1925; (Part II.), Barkla & Khastgir, Phil. Mag. Nov. 1925; "The Coherence of Superposed X-Radiations," Barkla & G. Mackenzie, 'Nature,' June 20, 1925, and earlier papers referred to.

Errata: Part I. *For* values of $\left(\frac{\mu}{\rho}\right)_{Cu}$ in figs. 10 & 11, *read* 10 times these values: thus, *for* 1·0 *read* 10; p. 1037, line 27, *for* 1921 *read* 1917; p. 1051, under J_1 Absorption Steps, *for* S = 3·5 *read* Cu = 3·5.

constitution of the two beams should show itself by a change in the ratio.

Now according to Compton's hypothesis, if λ be the wave-length of a primary radiation the modified scattered radiation should be of wave-length $\lambda + \cdot 024(1 - \cos\theta)$; hence in the two directions studied the wave-lengths should differ by ·024 Å.U. Over a range of wave-lengths from ·6 Å.U. to ·3 Å.U.—a quite normal range—the difference should vary from 4 per cent. to 8 per cent., and the absorption coefficients should differ by an amount varying from 12 per cent. to 20 per cent. approximately. This is a large difference ; one-tenth part of it should be easily measurable.

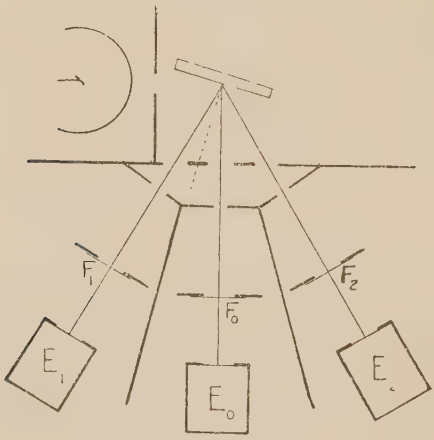
Fig. 1.



It is readily seen that, quite apart from any possible difference of wave-length produced in the two scattered beams proceeding in different directions, unless the primary beam is really homogeneous, a difference in the constitution of the two beams may arise from unequal filtering on emerging from the scattering plate. This, however, is easily eliminated, as in the experiments of Barkla & Ayres on the distribution of scattered radiation, by arranging that the scattered beams studied shall make equal angles with the normal to the scattering plate, and pass through equal thicknesses of that plate. This has been arranged in the later experiments. But even this precaution is unnecessary if either a very thin or a very thick sheet of scattering substance is used. It is unnecessary, too, in a substance consisting of very light atoms, for in this there is very little

selection of constituent radiations, the absorption of the different constituents varying very little with wave-length of the radiation : such a substance is paraffin wax. Consequently, in these earlier experiments with paraffin wax, and even with aluminium as scattering substances, there was little effect of difference of obliquity of the two scattered beams ; and what there was would tend to increase the difference of absorbability as expected in these two directions on A. H. Compton's hypothesis. It was in order to make the conditions as simple as possible, and to remove all possibility of the effect of unknown quantities, that we more recently arranged that the two directions of the scattered radiations tested should make the same angle with the normal, and so pass through equal thicknesses of absorbing substances, as do the beams entering electroscopes E_0 and E_1

Fig 2.



in fig. 2. The results of the two sets of experiments are identical in nature.

We obtained such an interesting series of results with the arrangement of fig. 1, that we give an account of them below. Fig. 3 shows the results of fifteen consecutive series of experiments. In each series the ratio of ionizations I_1/I_2 produced in the two electroscopes E_1 and E_2 was obtained when no intercepting sheet was placed in their path ; then the ratio of ionizations for equal and increasing thicknesses of aluminium placed in the two beams. In fig. 3 the ratio of ionizations I_1/I_2 is plotted against thickness of

absorbing aluminium. The remarkable features shown are the following:—

(1) In all the long series of fifteen experiments, fourteen

Fig. 3.

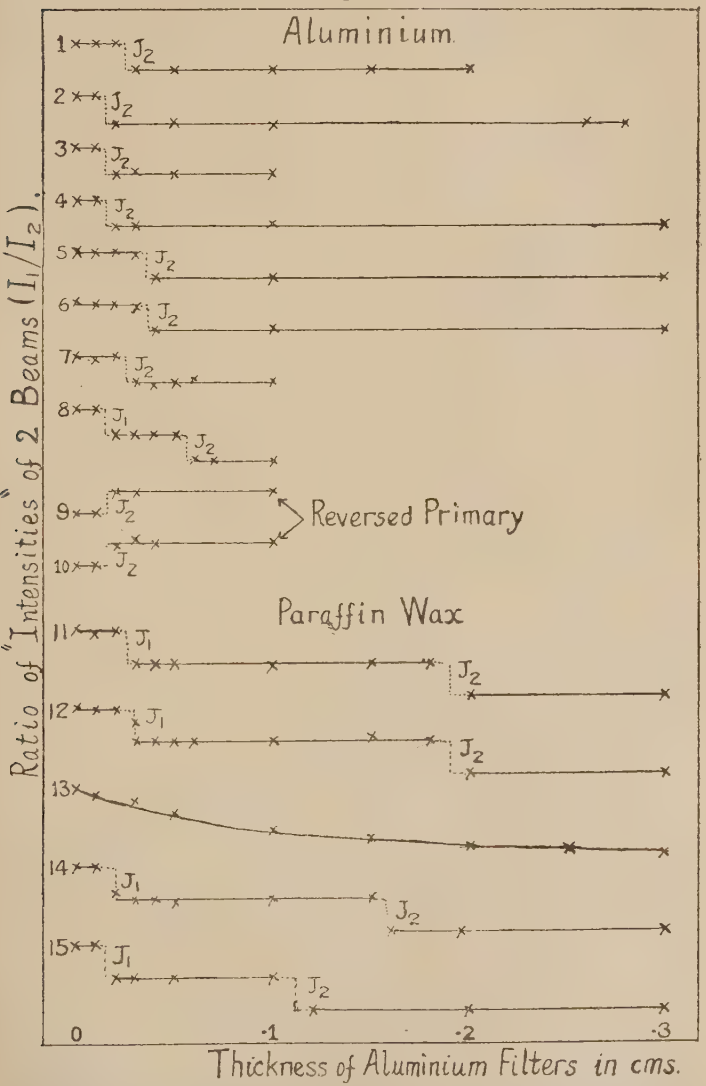


exhibit no difference between the two scattered beams except at the J discontinuities; this is shown by the horizontality of the lines indicating that one beam is absorbed exactly

as the other. In some of these experiments as much as about 75 per cent. of the total ionization was cut off between the discontinuities, so that the test of equality of penetrating power was a very sensitive one. A 2 per cent. difference of absorption coefficient would have been easily observed. Compton's "modified radiation" would give a 15 per cent. to 20 per cent. difference; if such a modified radiation had been present it could not have been more than 10 per cent. (probably much less) of the whole scattered radiation. There is no evidence of its existence at all.

(2) In all these experiments, however (all excepting Experiment 13), the J discontinuities were shown by *one* scattered beam but not by the other. The beam showing the discontinuities was the beam at an angle of 120° with the primary, for this beam exhibited a sudden *diminution* of intensity relative to the other. That is, the beam proceeding somewhat backward upon the primary showed at certain critical thicknesses of filtering aluminium the sudden diminution of intensity; the scattered beam proceeding somewhat forward did not show this. This was confirmed by simultaneous measurements in three directions. When the direction of the primary was reversed, *i. e.* the X-ray tube was placed on the other side of the scattering plate while everything else was unchanged, then the other electroscope E_2 showed the discontinuity, for the ratio I_1/I_2 as previously measured suddenly *rose* at the J discontinuity (see Experiments 9 & 10, fig. 3). This experiment showed that the occurrence of the discontinuity in the beam at an angle of 120° with the primary was not due to any peculiarity of situation or configuration, except with regard to the primary radiation.

In the whole series of experiments, with the exception of No. 13, not a single J discontinuity was missed.

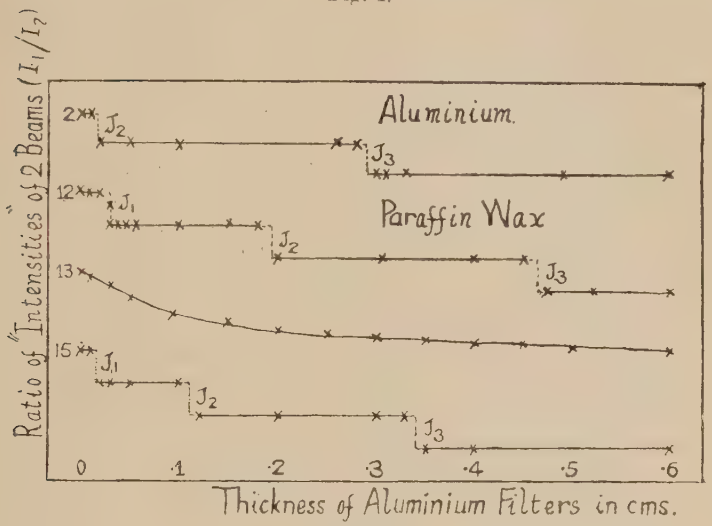
The values of the absorption coefficient $\left(\frac{\mu}{\rho} \text{ in Al}\right)$ calculated from a 50 per cent. "absorption" of the beam which gave the discontinuity, agreed remarkably well with those previously obtained for beams of various kinds. Thus the values for the J_1, J_2, and J_3 discontinuities respectively were :—

J_1	3·6, 3·6, 3·6, 3·7, 3·6,	average 3·6.
J_2	1·85, 1·9, 2, 2·1, 2·1, 2·1, 1·95, 1·9, 2, 2, 1·9, 2, 2, 2,	average 2.
J_3	·71, ·75, ·8,	average ·75.

as compared with 3·8, 1·9, and 0·7 previously published.

The three discontinuities were, however, in our experiments obtained by filtering *one* complex radiation, the three discontinuities appearing one after the other in the appropriate positions. The results of these more extensive series of filtering experiments are shown in fig. 4.

Fig. 4.



The magnitude of the discontinuities in the absorption of the radiations scattered from aluminium was exhibited by a sudden drop of about 7·5 per cent. in the ionization produced in the electroscope; when paraffin wax was used as scattering substance the magnitude was about 10 per cent.

Thus, although the two beams from paraffin wax, for instance, were normally absorbed at the same rate (see Experiments 11, 12, 14, 15 in fig. 3), the beam making an angle of 120° with the primary showed these three sudden falls in ionizing power when the values of $\frac{\mu}{\rho}$ (calculated from a 50 per cent. absorption, or rather 50 per cent. diminution in ionization) were 3·6, 2·0, and 0·75, and the whole beam had its ionizing action cut down by about 27 per cent. relative to the beam scattered at 60°. (It seems probable that if the filtering could have been carried further, the J_4 and J_5 discontinuities would also have occurred; and there is no reason to think that even the J_5 discontinuity is

the last) *. Thus, though between these J discontinuities the absorption coefficients of the two scattered radiations are identical, there is some quality of the radiation which causes the intensity of one radiation during transmission to fall abruptly when certain average penetrating powers are reached. We, of course, usually attribute such a drop in intensity, as measured in an electroscope, to an increase in absorption in the substance traversed. That this is so is evident from the fact that the aluminium or other absorbing substance does emit an increased electronic radiation—there is a true absorption of energy †.

When the primary beam was "softened," the filtering had to proceed a little further before the critical absorbability was reached; when "hardened" the discontinuity occurred earlier in the filtering process. This is seen by a comparison of the positions of the discontinuities in fig. 3 with the corresponding absorption coefficients of the *unintercepted* beams given in Column 4 of Table I., in which the results are collected. The position of the discontinuities was thus under control, as will be further demonstrated below.

Now it is perfectly evident that the sudden absorption occurring in a heterogeneous beam as it is filtered is not due to the appearance of any particular wave-length in the filtered radiation. On the other hand, these sudden increases in the absorption occur so persistently at very definite absorption coefficients, though this appears to be only an average absorption coefficient, that we are driven (not by these experiments alone, but by scores of experiments illustrating the same feature) to the conclusion that this so-called absorption coefficient indicates something much more fundamental than has hitherto appeared. For some years we were unprepared to accept the conclusion; it appeared to have no very definite physical significance. In many ways, however, wave-length is shown to be totally irrelevant except by its association with a certain absorption.

As we have pointed out previously in this connexion, temperature is likewise only an average, and the properties of substances depend, not on the energies of individual molecules, but on the average energy.

The sudden disappearance of energy from the beam of X-rays and appearance of energy in electrons of the transmitted substance indicates a concentration of the energy of

* This experiment shows how the dissymmetry of the scattered radiation on the two sides of the plane normal to the direction of primary propagation develops.

† See Bakerian Lecture, 1916 (Phil. Trans. 1917); other results unpublished.

the beam in certain atoms of the substance traversed, or whatever view we hold regarding radiation, it is a change of state of the energy of radiation. But certain conditions are necessary for the concentration of energy, as certain nuclei are essential to the condensation of a vapour. What under some conditions takes place continuously, under other conditions occurs discontinuously. This is well illustrated

TABLE I.

Number of Experiment.	Scattering Substance.	Thickness of Scatterer.	"Absorption Coefficients" of Unintercepted Radiations $\left(\frac{\mu}{\rho}\right)_{Al}$.	"Absorption Coefficients" at J Discontinuities. $\left(\frac{\mu}{\rho}\right)_{Al}$ J_1.	$\left(\frac{\mu}{\rho}\right)_{Al}$ J_2.	$\left(\frac{\mu}{\rho}\right)_{Al}$ J_3.
1	Aluminium	1·9 cm.	2·8	...	1·85	
2	,,	,,	2·5	...	1·9	·71
3	,,	,,	2·5	...	2	
4	,,	,,	2·6	...	2·1	
5	,,	·6 cm.	3·4	...	2·1	
6	,,	·3 cm.	3·5	...	2·1	
7	,,	1·9 cm.	3·0	...	1·95	
8	,,	·3 cm.	4·0	3·6	1·9	
9	,,	,,	2·6	...	2	
10	,,	,,	2·6	...	2	
11	Paraffin Wax	1·7 cm.	4·3	3·6	1·9	
12	,,	,,	4·5	3·6	2	·75
13	,,	,,	4·4			
14	,,	,,	4·3	3·7	2	
15	,,	·7 cm.	4·6	3·6	2	·8

by the results of Experiment 13 and other experiments, in which the difference between the two secondary beams is shown by the *continuously* greater absorption of the beam at 120°; this is indicated by a continuous curve sloping down to the right. What in Experiment 13 takes place continuously, in other experiments takes place in jumps, and these jumps occur at definite absorbabilities. But the strange feature is that we are not yet able to recognize any difference between Experiment 13 and Experiments 12 and 14 except in the result. Clearly in *all* of these experiments there is a difference between the two scattered beams, but

in one case it remains latent until these critical absorbabilities are reached.

It should be added that we have more recently obtained series of consecutive experimental results of both kinds—those showing a difference between the two beams by discontinuities and those showing a difference continuously *.

In a discussion of the theory of X-ray scattering, two cases (*a*) and (*b*) have thus again to be considered, as in the comparison of the radiation scattered at 90° with the primary radiation (Phil. Mag. Nov. 1925).

In *Case a* the difference between the scattered beams is shown only by discontinuities in the absorption of the radiation scattered at 120° ; otherwise no difference appears. In this case there is definitely no difference of wave-length if, as is usually assumed, the absorbability and general activity of an X-radiation depend only upon wave-length or frequency. But we have shown that a change of absorption and the associated phenomena do occur without a change of wave-length. Can a change in wave-length occur without a change in absorbability, etc.? Our results classified as *Case a* are only reconcilable with a change of wave-length if the activity of an X-radiation depends fundamentally on something other than waves, for we certainly do not get the change of properties which normally accompany a change of wave-length.

In *Case b*, illustrated by Experiment 13, in which the two scattered beams differ in absorbability, there might be a difference of wave-length between the two scattered beams, if further experiments did not indicate otherwise. But as we have found that a similar difference of absorbability sometimes appears between the scattered and the primary radiation—a difference which cannot depend primarily upon a change of wave-length, for it is shown in some substances when not in others,—we must conclude that the difference appearing in these experiments between the two scattered beams is not due to a difference in wave-length.

The plain fact is, that having shown the detachment of X-ray phenomena from mere frequency, it seems just possible that diffraction methods indicate a change of wave-length, whereas our methods indicate no corresponding change of properties, because those properties are not fundamentally and inseparably associated with waves. But it is not our intention in this paper to explore the whole range of

* In addition to those showing no difference whatever between the two scattered beams.

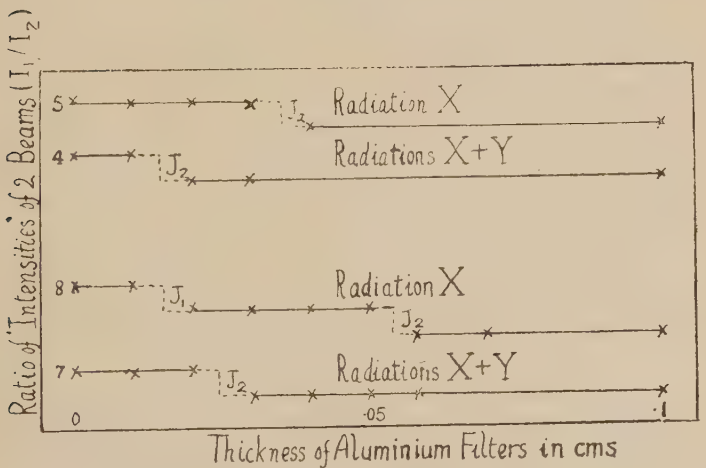
possibilities, logical and illogical: further experiments alone will enable us to solve these fundamental problems.

For the present we can say that if measured by the general activity (as distinct from the activity in particular substances) there is no difference of wave-length between the two radiations.

Superposition of Two Beams of X-rays.

That the J absorption and all the associated phenomena depend on the whole of a complex beam, and not on any of its components or even any group of its components, is shown most directly by the following experiments. A thin sheet of scattering aluminium was placed in position as before, and the thickness of filtering aluminium at which the J discontinuity occurred was found. When a thicker sheet of scattering substance was placed behind the first so that

Fig. 5.



there was superposed on the radiation previously experimented upon a more penetrating radiation from deeper layers, it was found that the first discontinuity had disappeared, but that in its place, that is at a thickness of filtering aluminium appropriate to the complex beam as a whole, there appeared the full discontinuity.

Thus Experiment 5, fig. 5, was made with a scattering sheet of aluminium ·6 cm. in thickness, and showed the J_2 discontinuity at a thickness of filtering aluminium between ·03 and ·04 cm., whereas when the thickness of scattering

aluminium was increased to 1·9 cm. and the ionization in the electroscope was (roughly) doubled, the J_2 discontinuity occurred for a thickness of filtering aluminium between the ·01 and ·02 cm. (Experiment 4, fig. 5). In order to avoid any possible effect due to a change in the primary radiation, the readings with the two thicknesses of scattering substance were taken in alternate pairs, so that corresponding points were obtained with practically identical radiations. A similar method was adopted in Experiments 8 and 7. It may be noticed that in Experiment 8 (fig. 5), with the thin sheet only ·3 cm. in thickness, the scattered beam was sufficiently soft to show the J_1 discontinuity in addition to J_2. With the additional thickness of 1·6 cm. of scattering aluminium, making a total thickness of 1·9 cm. (that is, in Experiment 7), the J_1 discontinuity was driven out of the range of experiments, and the J_2 discontinuity was displaced from a thickness between ·05 and 06 cm. to between ·02 and ·03 cm. No more direct experiment could be devised to show the coherence of constituent radiations. By this we mean that the J phenomenon is independent of individual harmonic constituents of a radiation, but dependent on the combination.

It is important to determine what conditions are necessary for the coherence of a complex beam. Must the two constituent beams be excited by the same primary beam, and must they be excited in the same substance? This point is at present under investigation, but it may be said that in preliminary experiments, when the first layers were of paraffin wax and the deeper layers of aluminium, there certainly was not the simple coalescence described above.

In addition, we have had scattered radiations excited by the same primary beam from air and from paper proceeding at the same time into the same electroscope in practically the same direction. The radiation from air was like the primary, that from paper was unlike. Thus these two beams appeared entirely independent.

Summary.

Three J discontinuities, J_1, J_2, and J_3, have been obtained in the absorption of one complex beam of X-rays by placing a gradually increasing thickness of aluminium in the path of the beam. (These were originally discovered by a quite different method and with different radiations—J_1 with scattered X-rays, J_2 with characteristic rays of the K series, J_3 with primary rays.)

It has also been shown by the superposition of two scattered radiations that the activity of the compound radiation is not the sum of the activities of the two constituent radiations. Further than that, each beam, as far as the J phenomenon is concerned, acts as a whole, and the compound beam, consisting of the two, behaves as a radiation of intermediate absorbability, showing not two di-continuities for the constituent beams, but one appropriate to the beam as a whole.

The activity of a radiation thus depends, in part at least, on something analogous to temperature of the radiation as a whole. This shows the separation of the activity of X-rays from the frequency or wave-length of the radiation, and illustrates the coherence of constituent radiations. It suggests the separation of quantum actions from the frequency with which they have always been associated.

Two beams of X-rays scattered in directions making angles 60° and 120° with the primary radiation differ, when at all, in one of two ways—(*a*) by the beam at 120° showing the J discontinuities, the other not (otherwise there is no difference of absorbability) ; or (*b*) by a continuous difference of absorbability in *some* substances. Neither of these can be reconciled with a true difference of wave-length, unless a change of wave-length can occur without the usual accompanying change in absorbability and general properties in *all* substances.

XLVI. *Properties of the Generalized Artificial Line.*

By The Research Staff of the General Electric Co., Ltd.*
(*Work conducted by* A. C. Bartlett.)

Summary.

It is shown that there exists a "Bridge" type artificial line section equivalent to the generalized artificial line section, and that results similar to those given previously for the Π and T section line (Phil. Mag. April 1925) hold for the generalized artificial line.

THE theory has already been given † of a generalized artificial line constructed of sections such as fig. 1, where each section is symmetrical about a centre element x_n which will be either shunt or series according as n is even or odd.

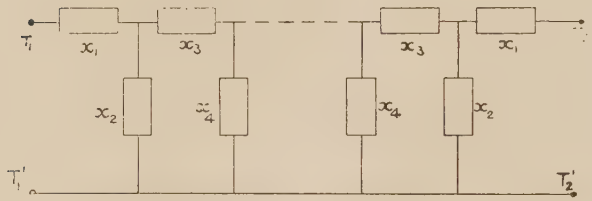
* Communicated by the Director.

† Phil. Mag. xxxix. p. 1072 (May 1925).

It was shown that, if the impedances of x_1, x_3, etc. are a_1, a_3, etc., and the impedances of x_2, x_4 are $\frac{1}{a_2}$, $\frac{1}{a_4}$, etc., the line characteristic impedance of the artificial line is given by

$$\sqrt{\frac{K(a_1, a_2 \ldots, a_n, \ldots a_2, a_1)}{K(a_2, a_3 \ldots, a_n, \ldots a_3, a_2)}}.$$

Fig. 1.



A property of continuants is that

$$K(a_1, a_2 \ldots, a_n, \ldots a_2, a_1) = 2K(a_1, a_2 \ldots, a_{n-1}\ K\left(a_1, a_2 \ldots, a_{n-1}, \frac{a_n}{2}\right),$$

and applying this to both numerator and denominator,

$$Z_0 = \sqrt{\frac{K(a_1, a_2 \ldots a_{n-1})\ K\left(a_1, a_2 \ldots, a_{n-1}, \frac{a_n}{2}\right)}{K(a_2, a_3 \ldots a_{n-1})\ K\left(a_2, a_3 \ldots, a_{n-1}, \frac{a_n}{2}\right)}},$$

which is of the form:

$$Z_0 = \sqrt{P \times Q},$$

where

$$P = \frac{K(a_1, a_2 \ldots, a_{n-1})}{K(a_2, a_3 \ldots, a_{n-1})},$$

$$Q = \frac{K\left(a_1, a_2 \ldots, a_{n-1}, \frac{a_n}{2}\right)}{K\left(a_2, a_3 \ldots, a_{n-1}, \frac{a_n}{2}\right)}.$$

P and Q are obviously impedances; P is the impedance of the network of fig. 2 (*a*) if n is even, and of fig. 2 (*b*) if n is odd; Q is the impedance of the network of fig. 3 (*a*) if n is even, and of fig. 3 (*b*) if n is odd.

Fig. 2.

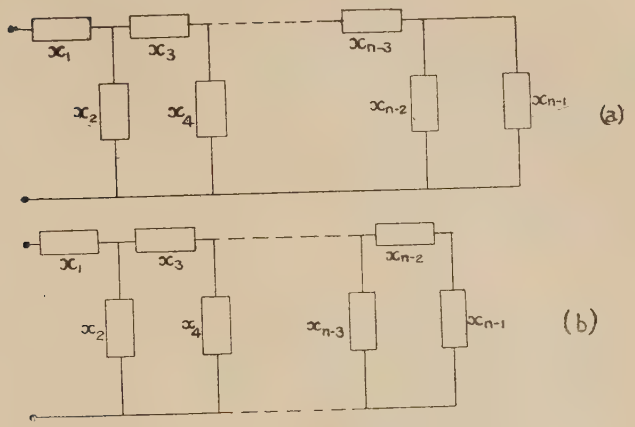
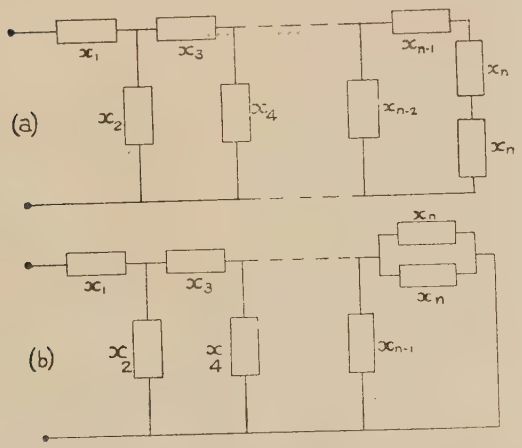


Fig. 3



A bridge section having arms P and Q will thus have the same line characteristic impedance as the original section. If its propagation constant is ϕ,

$$Z_0 \tanh \phi = \frac{2}{\frac{1}{Z_0 \coth \frac{\phi}{2}} + \frac{1}{Z_0 \tanh \frac{\phi}{2}}}$$

$$= \frac{2}{1/P + 1/Q}.$$

On inserting values of P and Q this is found to be equal to

$$\frac{K(a_1, \ldots a_n, \ldots a_1)}{K(a_2, \ldots a_n, \ldots a_1)},$$

which is $Z_0 \tanh \theta$ where θ is the propagation constant of the original line.

Thus the bridge section with arms P and Q has the same line characteristic impedance and the same propagation constant as the original section, and is identically equivalent to it. P and Q must therefore have the values

$$Z_0 \tanh \frac{\theta}{2} \quad \text{and} \quad Z_0 \coth \frac{\theta}{2}$$

but it has still to be determined which is the value of P and which is the value of Q; that is to say, there is an uncertainty which of the output terminals of the bridge section correspond to which of the original section.

The receiving end impedance of one section of the original artificial line short-circuited at the far end is $Z_0 \sinh \theta$, which from first principles is

$$K(a_1 \ldots a_n, \ldots a_1).$$

Assuming, first, that

$$P = Z_0 \coth \frac{\theta}{2} \quad \text{and} \quad Q = Z_0 \tanh \frac{\theta}{2};$$

then

$$\begin{aligned} Z_0 \sinh \theta &= \frac{1}{Z_0 \tanh \frac{\theta}{2} + Z_0 \coth \frac{\theta}{2}} \\ &= \frac{1}{2} \cdot \frac{1}{\frac{1}{Q} + \frac{1}{P}} \\ &= (-1)^{n-1} K(a_1, \ldots a_n \ldots a_1). \end{aligned}$$

This is equal to the value previously obtained only if n is odd. Hence, when n is odd,

$$P = Z_0 \coth \frac{\theta}{2},$$

$$Q = Z_0 \tanh \frac{\theta}{2};$$

and similarly when n is even

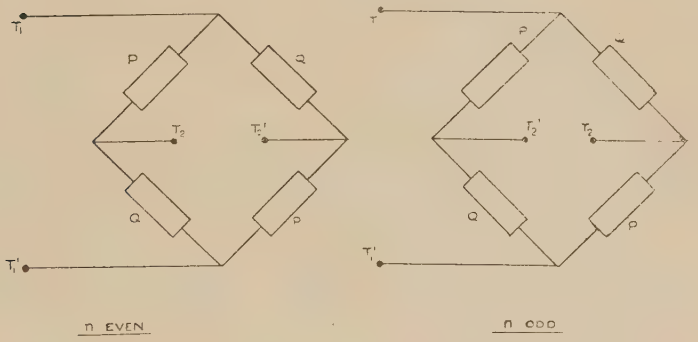
$$P = Z_0 \tanh \frac{\theta}{2},$$

$$Q = Z_0 \coth \frac{\theta}{2}.$$

Thus the correspondence of the terminals is as shown in fig. 4.

The original section can be cut exactly into halves by replacing the central impedance by two impedances of half its value in series if n is odd, or by two impedances of double its value in parallel if n is even. It is interesting to note

Fig. 4.



that, whether n is odd or even, $Z_0 \coth \frac{\theta}{2}$ is then the impedance of a half section open circuited at the far end and $Z_0 \tanh \frac{\theta}{2}$ is the impedance of a half section short-circuited at the far end.

It is further seen that, since the impedances $Z \coth \theta$, $Z_0 \tanh \theta$, $Z_0 \coth \frac{\theta}{2}$, $Z_0 \tanh \frac{\theta}{2}$ can be constructed, the results previously given * for the simple Π and Γ sections also hold for the generalized artificial line.

Thus there exist a number of alternative networks that have the same impedance as an artificial line made up of any number of sections short-, or open-circuited at the far end or terminated by $Z \tanh \frac{\theta}{2}$ or $Z_0 \coth \frac{\theta}{2}$. Further, a single bridge type section can be constructed in a number of ways so as to be equivalent both as regards input and output terminals to an artificial line consisting of any number of sections.

* Phil. Mag. xlix. p. 728 (April 1925).

XLVII. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from ser. 6, vol. 50, p. 1298.]

May 6th, 1925.—Dr. J. W. Evans, C.B.E., F.R.S., President, in the Chair.

Mr. Edward Battersby Bailey, M.C., B.A., F.R.S.E., F.G.S., delivered a lecture on the Tertiary Igneous Geology of the Island of Mull, illustrated by lantern-slides.

He asked his hearers to remember that he was only one of a small group of workers who had recently been employed in adding to our knowledge of the geology of Mull. In the Geological Survey Memoir (1924), the share of each participant is indicated by initials.

The columnar lavas of Staffa and South-Western Mull were described, with especial reference to Scrope's double-tier jointing. Iddings's explanation of the apparent repugnance of approaching columns, and Macculloch's tree that stands upright although submerged in lava.

Attention was then focussed upon Judd's region of central pneumatolysis (propylitization), where, within an area measuring 15 miles in diameter, it is impossible to find a lava that has retained its olivine undecomposed.

Judd's conception of central subsidence was next discussed. It now appears, from the disposition of lava-types and other considerations, that central subsidence culminates in two adjacent calderas. The occurrence of many pillow-lavas within one of these calderas—at the centre of a manifestly terrestrial volcano—points to the frequent presence of a crater-lake. The crater-hollow must have been renewed by intermittent subsidence—for instance, Kilauea and Askja. The rim-craters of Askja may be taken as a surface-manifestation of a ring-dyke. Ring-dykes are numerous in Mull, where their most perfect example is the Loch Ba felsite, traced by Mr. W. B. Wright and Mr. J. E. Richey. Ring-dykes are known at other British Tertiary centres, and also at Glen Coe and Ben Nevis. Many ring-structures occur in Iceland, in addition to the Askja caldera, and have been described by Thoroddsen. At Oslo they appear in Brögger & Scheteli's map (1923).

There is conspicuous folding in Mull attributable to the lateral expansion of an early ring-dyke. Similar folding does not recur in connexion with later ring-dykes. These may, in some cases, have made room for themselves by stoping en masse, and in others by pushing country-rock inwards towards a central orifice.

Several ring-dykes in Mull show gravitational differentiation, and the lecturer explained that he had been convinced by Dr. H. H. Thomas and Mr. A. F. Hallimond that this had taken place during crystallization.

Cone-sheets were passed in review, and emphasis laid on their great aggregate bulk.

Finally, the Mull swarm of north-westerly dykes was considered. The dyke-swarm owes its location to the previous development of the central conduit. One of its members, with ash-vents distributed along its course, has furnished Dr. B. N. Peach and others with a convincing analogue of the Laki fissure in Iceland. Probably, many of the Mull dykes fed fissure-eruptions, as Sir Archibald Geikie long ago maintained; but the products of most, if not all, of these eruptions have been eroded away.

June 16th.—Dr. J. W. Evans, C.B.E., F.R.S., President, in the Chair.

The following communication was read:—

'On some Occurrences of Spherulitic Siderite and other Carbonates in Sediments'. By Edmondson Spencer, B.Sc., Ph.D., F.G.S.

The author gives descriptions of a number of spherulitic aggregates (many of which have been described as oolitic) in freshwater clays and in coals. The occurrences, which are considered in detail, include those in the Fairlight Beds, the Upper Coal Measures of Staffordshire and South Wales, the Upper Wankie Sandstone Series (Rhodesia), and the coals of the Damuda Basin (India). For comparison with these, spherulites with radiolaria from Santo Domingo (Portugal) are described.

The spherulites are composed of rhombohedral carbonates, usually siderite, but occasionally of calcite, sideroplesite, dolomite, or a mixture of manganese and iron carbonates (as at Santo Domingo). By treating thin slides of the spherulitic siderite (after heating to redness) with warm hydrochloric acid and stannous chloride, the iron is removed and the structure, as outlined by occluded sedimentary material (such as clay or coal), may be studied.

Certain common characters are observed: (1) The spherulites occur in association with fine-grained sediments of carbonaceous,

muddy, or silty type, often with comminuted plant-tissue; (2) the deposits seem, without exception, to be of freshwater origin and devoid of calcareous shelly remains; (3) the carbonate material in most cases consists of nearly pure siderite, with a little carbonate of magnesium and calcium (usually in dolomite-proportions); (4) the spherulites are fairly uniform in size locally: the smallest series has a diameter of about 0·5 mm. and the largest series 2 to 3 mm.; (5) the occluded sediment is similar to that in which the spherulites are embedded, and has been enclosed during their growth; and (6) where 'zoning' of the sediment occurs, it is subordinate to radial structure.

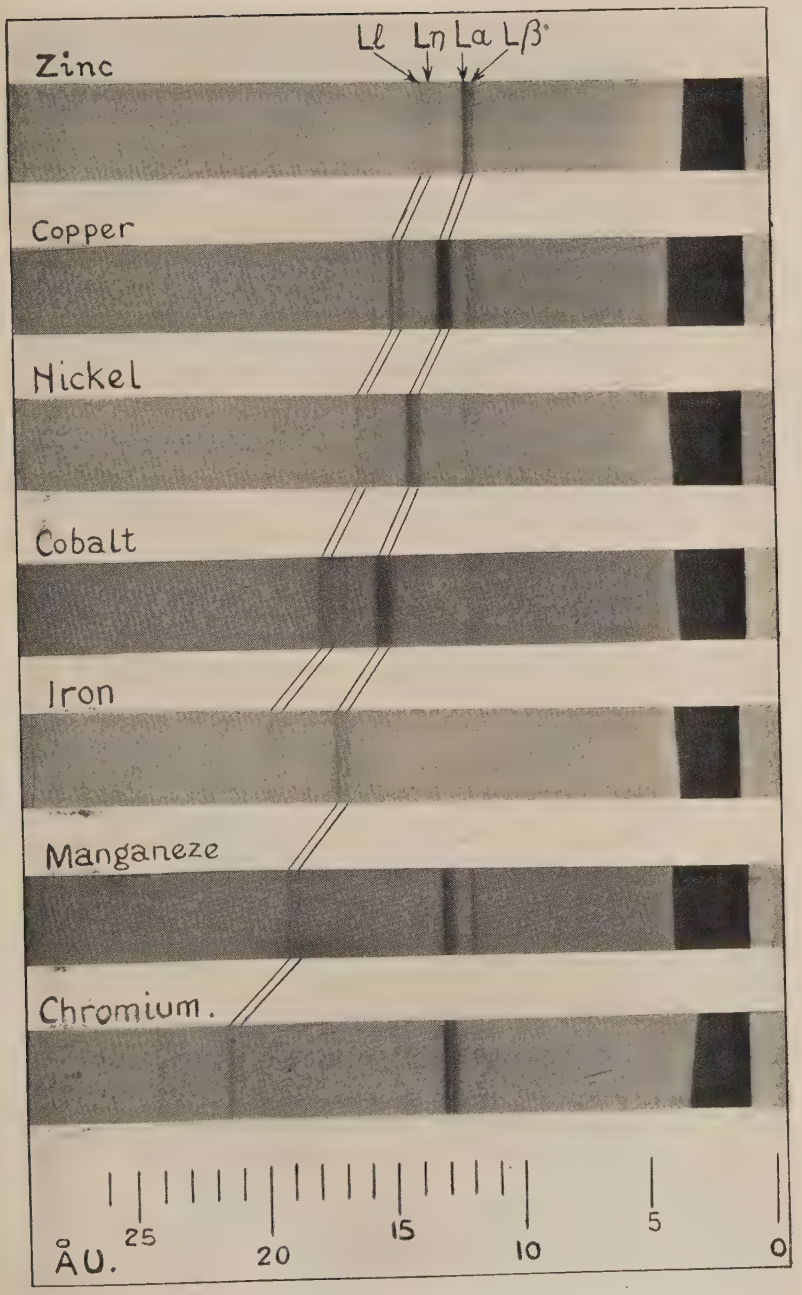
It is concluded that the spherulites have formed from iron-carbonate solutions held within the gradually settling and consolidating sediment. The contrast in the character of carbonate chemically precipitated from solution (as in the blackband and clay-ironstones) is noted.

The reactions resulting from the presence in sediments of humate compounds, salt, calcium carbonate, etc. are considered. The author believes that the iron compounds present in solution in fresh water as carbonates, humates, or hydrolized and possibly colloidal hydrates, were adsorbed by the fine-grained and partly colloidal sediments, and were carried down with them during deposition. Conditions of supersaturation would result from the settling and flocculation of the sediment, and from the gradual upward expulsion of the more readily diffused water-molecules. Crystallization would then commence at a number of centres simultaneously, the spherulitic growth ceasing before the consolidation of the sediment was completed. Comparisons are instituted with well-known diffusion phenomena in colloidal media resulting in the production of 'zoning'.

Interfering surfaces between adjoining spherulites are mostly plane, but occasionally are slightly concave to the smaller individuals.

In an Appendix, the author discusses mathematically the form of the surface of contact between spherulites, as determined by various rates of growth.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]


Lℓ
Lη
Lα
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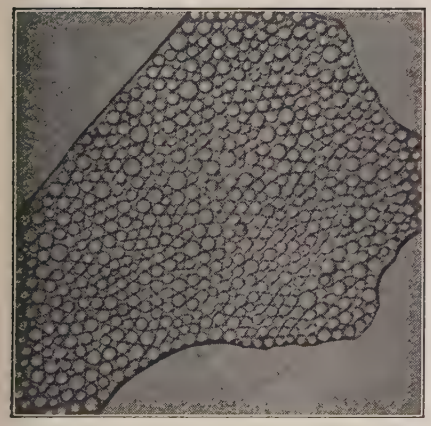


Fig. 1.

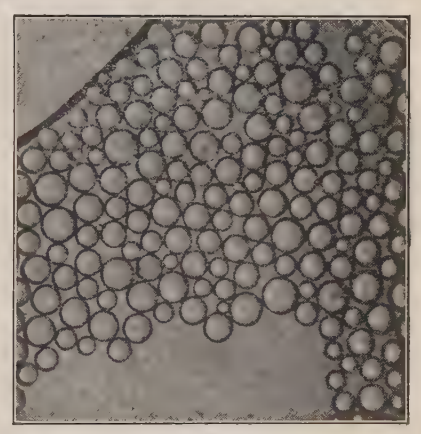


Fig. 2.

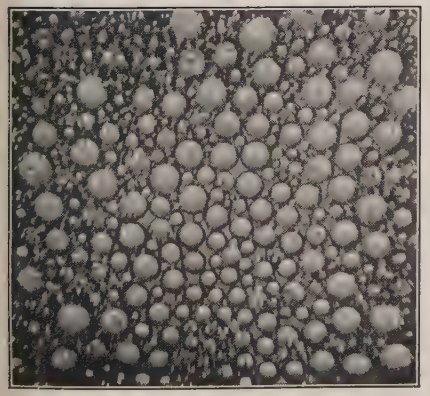


Fig. 3.

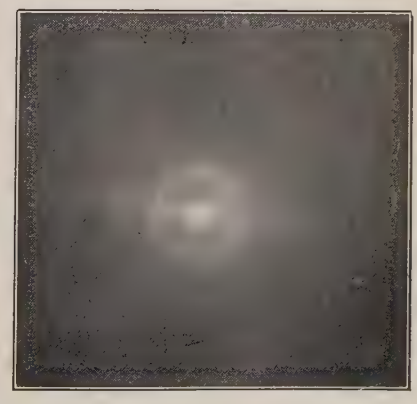
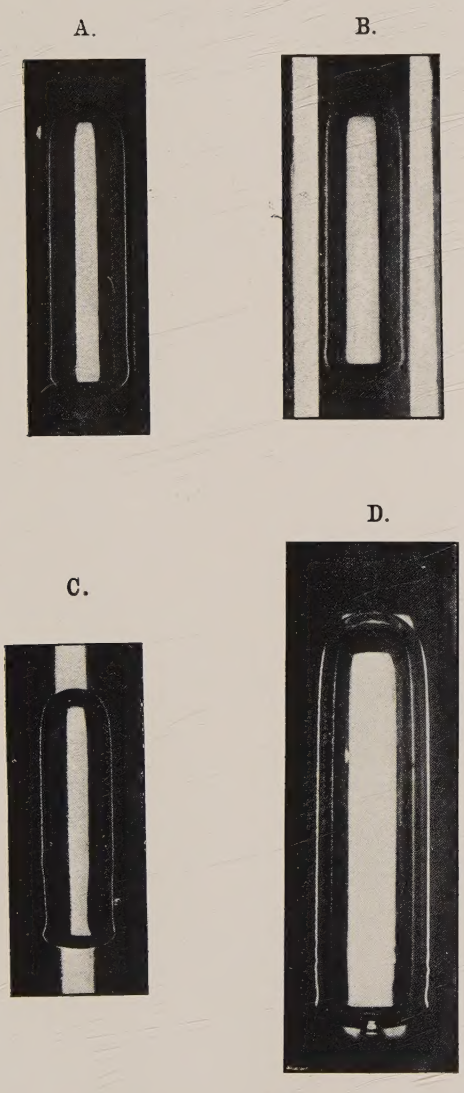


Fig. 4.

Chromatic Emulsions.

FIG. 2.



A & B. Machine Oil in tube 0·646 cm. diam.
(The tube was differently masked to define outline of the bubble.)

C. Water in tube 0·646 cm. diam.

D. Water in tube 1·0 cm. diam.

Water-spark absorption spectrum of iron.
(3rd order.)